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OXFORD IB DIPLOMA PROGRAMME



ANSWERS

2014 EDITION

CHEMISTRY

COURSE COMPANION

Sergey Bylikin
Gary Horner
Brian Murphy
David Tarcy

OXFORD



Topic 1 – Stoichiometric relationships

Activity answers (possible responses could include the following)

Page 4

1. energy provided to the system is being used to break down the intermolecular hydrogen bonds between the H_2O (l) molecules; discussion of latent heat of vaporisation;
2. water vapour results in more painful burns to the skin; boiling water and water vapour both have a temperature of 100°C ; vaporisation is an endothermic process; condensation of water vapour on the skin is an exothermic process;
3. the heat from the sun and warm air passing over the body increases the rate of evaporation from the skin; evaporation is an endothermic process; water molecules leaving the surface of the skin results in a loss of energy from the skin; the response of the human body is to shiver;

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- a) yield examines the efficiency of the reaction in converting reactants to products under given conditions; it makes no distinction between useful products and waste products produced during a reaction; the atom economy may be poor if a reaction produces a high proportion of products with little or no commercial value or application;
- b) energy consumption and paper recycling industry; wood pulp, Green Chemistry, availability and reserves of reactant materials;

$$\begin{aligned} \text{c) percentage atom economy} &= \frac{\text{Molecular mass of atoms of useful products}}{\text{Molecular mass of atoms in reactants}} \times 100\% \\ &= \frac{M_r(\text{CH}_3(\text{CH}_2)_3\text{Br})}{(\text{Molecular mass of atoms in reactants})} \\ &= \frac{137.03}{(74.14 + 102.89 + 98.09)} \times 100\% = 49.8\% \end{aligned}$$

Quick questions

Page 7

1. $\text{Zn(s)} + 2\text{HCl(aq)} \rightarrow \text{ZnCl}_2\text{(aq)} + \text{H}_2\text{(g)}$
2. $2\text{H}_2\text{(g)} + \text{O}_2\text{(g)} \rightarrow 2\text{H}_2\text{O(g)}$
3. $\text{CaCO}_3\text{(s)} \xrightarrow{\Delta} \text{CaO(s)} + \text{CO}_2\text{(g)}$

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Type of reaction	Equation Number
Combination	1
Decomposition	2, 5, 9
Combustion	3, 4, 6
Double Replacement	8
Neutralization	7

1. $\text{SO}_3\text{(g)} + \text{H}_2\text{O(l)} \rightarrow \text{H}_2\text{SO}_4\text{(aq)}$
2. $2\text{NCl}_3\text{(g)} \rightarrow \text{N}_2\text{(g)} + 3\text{Cl}_2\text{(g)}$
3. $\text{CH}_4\text{(g)} + 2\text{O}_2\text{(g)} \rightarrow \text{CO}_2\text{(g)} + 2\text{H}_2\text{O(g)}$
4. $4\text{Al(s)} + 3\text{O}_2\text{(g)} \rightarrow 2\text{Al}_2\text{O}_3\text{(s)}$
5. $2\text{KClO}_3\text{(s)} \rightarrow 2\text{KCl(s)} + 3\text{O}_2\text{(g)}$



6. $\text{C}_3\text{H}_8(\text{g}) + 5\text{O}_2(\text{g}) \rightarrow 3\text{CO}_2(\text{g}) + 4\text{H}_2\text{O}(\text{g})$
7. $\text{Ni}(\text{OH})_2(\text{s}) + 2\text{HCl}(\text{aq}) \rightarrow \text{NiCl}_2(\text{aq}) + 2\text{H}_2\text{O}(\text{l})$
8. $2\text{AgNO}_3(\text{aq}) + \text{Cu}(\text{s}) \rightarrow \text{Cu}(\text{NO}_3)_2(\text{aq}) + 2\text{Ag}(\text{s})$
9. $\text{Ca}(\text{OH})_2(\text{s}) \rightarrow \text{CaO}(\text{s}) + \text{H}_2\text{O}(\text{l})$

Page 16

- a) $148.33 \text{ g mol}^{-1}$
- b) $105.99 \text{ g mol}^{-1}$
- c) $399.91 \text{ g mol}^{-1}$
- d) $256.56 \text{ g mol}^{-1}$
- e) 99.4 g mol^{-1}
- f) $162.12 \text{ g mol}^{-1}$
- g) 253.8 g mol^{-1}
- h) $246.52 \text{ g mol}^{-1}$
- i) 135.1 g mol^{-1}
- j) $141.94 \text{ g mol}^{-1}$

Page 17

1. a) $\frac{8.09}{26.98} = 0.30 \text{ mol}$
 b) $\frac{9.8}{98.09} = 0.01 \text{ mol}$
 c) $\frac{25.0}{100.09} = 0.25 \text{ mol}$
 d) $\frac{279.94}{399.91} = 0.70 \text{ mol}$
2. a) $0.150 \times 28.02 = 4.20 \text{ g}$
 b) $1.20 \times 64.07 = 76.9 \text{ g}$
 c) $0.710 \times 310.18 = 220 \text{ g}$
 d) $0.600 \times 60.06 = 36.0 \text{ g}$
3. a) $2.00 \times 6.02 \times 10^{23} = 1.20 \times 10^{24}$
 b) $0.200 \times 6.02 \times 10^{23} = 1.20 \times 10^{23}$
 c) $\frac{72.99}{162.2} \times 6.02 \times 10^{23} = 2.71 \times 10^{23}$
 b) $\frac{4.60}{46.01} \times 6.02 \times 10^{23} = 6.02 \times 10^{22}$

Page 22

1. a) O_2
 b) C_4H_{10}
 c) C_4H_{10}
 d) O_2
2. Na_2CO_3 is the limiting reagent; 5.0 g of CaCO_3
3. a) $4\text{KO}_2 + 2\text{CO}_2 \rightarrow 2\text{K}_2\text{CO}_3 + 2\text{O}_2$
 b) KO_2 is the limiting reagent
 c) $27.64 \text{ g K}_2\text{CO}_3$
 d) 9.600 g O_2



4. a) HNO_3 is in excess
b) 96.4 g
c) 9.34 g NO
5. a) MnO_2 is the limiting reagent
b) 88.81 %

Page 24

1. a) 4.0 g of $\text{C}_9\text{H}_8\text{O}_4$
b) Percentage yield 93%
2. 0.782 g of Na_2CO_3
3. a) Theoretical yield = 40.0 g
b) Percentage yield = 70%

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113.5 dm³ of NH_3 and 56.75 dm³ of CO_2

Page 33

1. a) 98.09 g of H_2SO_4
2. $1.6 \times 4 \times 2.5 \times 6.02 \times 10^{23} = 9.6 \times 10^{24}$



End of topic questions (page 34)

1. a) $26.60 - 25.32 = 1.280 \text{ g}$
 b) $\frac{1.220}{18.02} = 0.06770 \text{ mol}$
 c) $25.32 - 24.10 = 1.220 \text{ g}$
 d) $\frac{1.22}{120.38} = 0.01013 \text{ mol}$
 e) 1:6.683
 f) $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$
2. a) $\frac{1.17}{233.4} = 5.01 \times 10^{-3} \text{ mol}$ ($5.02 \times 10^{-3} \text{ mol}$ also acceptable)
 b) $5.01 \times 10^{-3} \text{ mol}$ ($5.02 \times 10^{-3} \text{ mol}$)
 c) $2.50 \times 10^{-3} \text{ mol}$ ($2.51 \times 10^{-3} \text{ mol}$)
 d) (i) Iron $55.85 \times 2.50 \times 10^{-3} = 0.140 \text{ g}$
 (ii) Ammonium $18.05 \times 5.01 \times 10^{-3} = 0.0904 \text{ g}$
 (iii) Sulfate $96.06 \times 5.01 \times 10^{-3} = 0.481 \text{ g}$
 e) $0.982 \text{ g} - 0.711 \text{ g} = 0.271 \text{ g H}_2\text{O}$;
 $\frac{0.271}{18.02} = 1.50 \times 10^{-2} \text{ mol}$
 f) $\frac{0.711}{284.07} = 2.50 \times 10^{-3} \text{ mol}$; $\frac{1.50 \times 10^{-2}}{2.50 \times 10^{-3}} = 6$
3. A
4. B
5. C
6. B
7. C
8. a) $n(\text{Cu}_2\text{O}) = \frac{10.0 \times 10^3}{143.1} = 69.9 \text{ mol}$
 $n(\text{Cu}_2\text{S}) = \frac{5.00 \times 10^3}{159.16} = 31.4 \text{ mol}$
 Cu_2S is the limiting reagent
 b) $n(\text{Cu}) = 6 \times n(\text{Cu}_2\text{S}) = 6 \times 31.4 = 188 \text{ mol}$
 $m(\text{Cu}) = 188 \times 63.55 = 11947 \text{ g}$ (11.9 kg);
9. a) $\frac{\text{C}}{12.01} = 5.16$ $\frac{\text{N}}{14.01} = 1.72$ $\frac{\text{H}}{1.01} = 13.8$;
 C_3NH_8 ;
 b) the average mass of a molecule compared to 1/12 of (the mass of) one atom of ^{12}C which by definition is taken as 12 **or**
 average mass of a molecule/mass of 1/12 of one atom of ^{12}C
 c) $\text{C}_6\text{N}_2\text{H}_{16}$
10. empirical formula = CN
 $M_r = 51.9 \text{ g mol}^{-1}$
 $:\text{N} \equiv \text{C} - \text{C} \equiv \text{N}:$



11. a) to prevent (re)oxidation of the copper

b) number of moles of oxygen = $\frac{1.60}{16.00} = 0.10$

number of moles of copper = $\frac{6.35}{63.55} = 0.10$

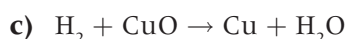
empirical formula = Cu (0.10) : O (0.10) = CuO

$\frac{6.35}{7.95} = 79.8\%$

$\frac{1.60}{7.95} = 20.2\%$

$\frac{70.8}{63.5} = 1.25$

$\frac{20.2}{16} = 1.29$



d) (black copper oxide) solid turns red/brown; condensation/water vapour (on sides of test tube);

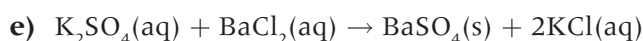
12. a) $M(\text{BaSO}_4) = 137.34 + 32.06 + 4 \times (16.00) = 233.40 \text{ g mol}^{-1}$

$n(\text{BaSO}_4) = \frac{0.672 \text{ g}}{233.40 \text{ g mol}^{-1}} = 0.00288 = 2.88 \times 10^{-3} \text{ mol}$

b) $n(\text{alkali metal sulfate}) = 0.00288 = 2.88 \times 10^{-3} \text{ mol}$

c) $M = \frac{m}{n} = \frac{0.502 \text{ g}}{0.00288 \text{ mol}} = 174.31 \text{ units: g mol}^{-1}$

d) $2(A_r) + 32 + 4(16) = 174$, thus $A_r = 39$ or $A_r = \frac{(174 - (32 + (4 \times 16)))}{2} = 39$; Potassium (K);



13. A. (i) $M_r(\text{C}_7\text{H}_6\text{O}_3) = 138.13 \text{ g mol}^{-1}$

$n = \frac{3.15}{138.13} = 2.28 \times 10^{-2} \text{ mol}$

(ii) $M_r(\text{C}_9\text{H}_8\text{O}_4) = 180.17 \text{ g mol}^{-1}$

$m = 180.17 \times 2.28 \times 10^{-2} = 4.11 \text{ g}$

(iii) percentage yield = $\frac{2.50}{4.11} \times 100 = 60.8\%$;

(iv) 3; percentage uncertainty = $\frac{0.02}{2.50} \times 100 = 0.80\%$

(v) sample contaminated with ethanoic acid / aspirin not dry / impure sample;

14. B. (i) $0.100 \times 0.0285 = 2.85 \times 10^{-3} \text{ mol}$

(ii) $2.85 \times 10^{-3} \text{ mol}$

(iii) $63.55 \times 2.85 \times 10^{-3} = 0.181 \text{ g}$

(iv) $\frac{0.181}{0.456} \times 100 = 39.7\%$

(v) $\frac{44.2 - 39.7}{44.2} \times 100 = \frac{10}{10.2}\%$



Topic 2 – Atomic structure

Quick question (page 39)

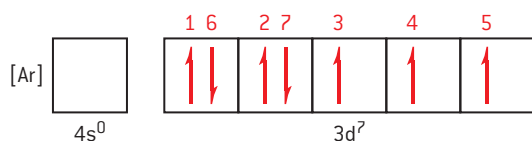
Both sulfur dioxide, SO_2 (g), and sulfur trioxide, SO_3 (g) are acidic oxides (Topic 3, page 87) with sulfur having a different oxidation numbers (Topic 9, page 213).

	SO_2		SO_3	
	S	O	S	O
A_r	32.07	16.00	32.07	16.00
Combined mass of individual atoms	32.07	$(16.00 \times 2) = 32.00$	32.07	$(16.00 \times 4) = 48.00$
Calculate ratio	$\frac{32.07}{32.07} = 1.000$	$\frac{32.00}{32.07} = 0.9978$	$\frac{32.07}{32.07} = 1.000$	$\frac{48.00}{32.07} = 1.497$
Ratio of the mass of oxygen per gram of sulfur	0.9978: 1.000 1:1 (Simplified)		1.497: 1.000 1.5:1 (Simplified)	

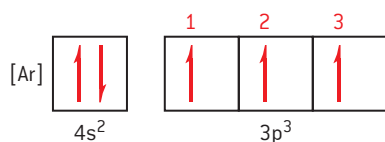


End of topic questions (page 65)

1. C; boron-11 has an atomic number of 5; this represents the number of protons found in the nucleus; an atom of the element boron also has the same number of electrons; the relative atomic mass represents the number of protons and neutrons; taking the difference between the two numbers calculates the number of neutrons in the nucleus, 6;
2. C; an atom of sulfur-34 has 16 protons, 16 electrons and 18 neutrons; an ion of sulfur with a 2-charge has an additional 2 electrons for a total number of 18 electrons;
3. A; statement III is not correct; isotopes of the same element have the same chemical properties but exhibit different physical properties due to differences in their mass numbers;
4. B; $(0.69 \times 63) + (0.31 \times 65) = 63.6$
5. A; $(0.80 \times 23) + (0.20 \times 28) = 24$
6. A; the relationship between wavelength, frequency and energy is the greater the energy, the shorter (smaller) the wavelength and the higher the frequency; ultraviolet light is high energy/short wavelength when compared to visible light; infrared light is lower energy/low frequency compare to visible light;
7. B; the series of lines found in the visible region of the spectrum is called the Balmer series; they are associated with electronic transitions from upper energy levels down to the $n = 2$ energy level;
8. D; the line emission spectrum of hydrogen provides evidence for the existence of electron in discrete energy levels, which converge at higher energies; high energy photons of light have a higher frequency and shorter wavelength;
9. B; the energy levels are split into sublevels, of which there are four common types: s,p,d and f; each has a characteristic shape and associated energy; the order of increasing energy is $s < p < d < f$;
10. C; cobalt (atomic number 27) has argon as its nearest noble gas core; the condensed electron configuration is a combination of the nearest noble gas core and the valance electrons of the element; when a transition element loses one or more electrons, they are removed from the orbital of highest principle quantum number, in this case the 4s; on removal of the three electrons, the resulting electron configuration of $4s^0 3d^6$;
11. see table and diagrams on page 54
12. a) $IV < I < II < III$
 - a continuous spectrum has all colors/wavelengths/frequencies whereas a line spectrum has only (lines of) sharp/discrete/specific colors/wavelengths/frequencies;
 - UV-B radiation has shorter wavelength; hence, has higher energy; increases risk of damage to skin cells / causes cancer;
13. a) Mn: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^5$
 Mn^{2+} : $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5$
 - $[Ar] 3d^9$
 - Co^{2+} : $[Ar] 3d^7$



As: $[Ar] 4s^2 4p^3$





14. Comment- Give a judgment based on a given statement or result of a calculation [Assessment Objective 3]

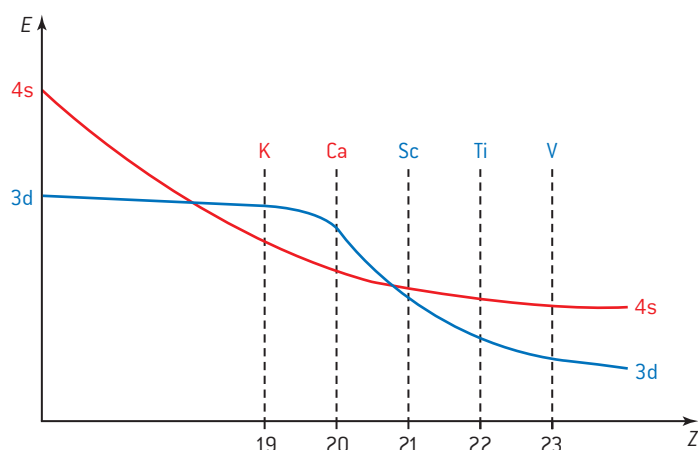
The Bohr theory provided a first approximation of atomic structure, and in particular the arrangement of electrons; it has since been replaced by more sophisticated mathematical theories from the field of quantum mechanics, which incorporate the wave-like nature of the electron; the wavefunctions of electrons in an atom are described by atomic orbitals; an orbital is a three-dimensional graph with a cluster of dots showing the probability of finding the electron at different distances from the nucleus; a boundary surface could be drawn around this cluster of dots to define a region of space where there is a 99% chance of finding the electron; atoms represented by spheres can be helpful in placing them as individual particles; it allows for structures of molecules to be represented as the joining of the particles; the sphere model can sometimes hinder interpretations as it implies a finite boundary surface;

15. Discuss - Offer a considered and balanced review that includes a range of arguments, factors or hypotheses. Opinions or conclusions should be presented clearly and supported by appropriate evidence. [Assessment Objective 3]

The Dalton model of the atom as an indivisible particles was changed as result of Thomson's experiment; without the use of high voltage cathode rays and magnetism, Thomson would not have been able to deduce that all electrons are similar and a part of each atom; his model further helped explain bonding by placing charges in atoms;

16. Suggest - Propose a solution, hypothesis or other possible answer. [Assessment Objective 3]

The plot of orbital energy (E) vs. atomic number (Z) for neutral atoms is shown below:



In vanadium, 3d electrons have lower orbital energy than 4s electrons, so the 3d subshell should be filled before the 4s subshell; however, the formula $[\text{Ar}]4s^23d^3$ implies the reverse order of orbital energies, i.e., $E(3s) < E(3d)$; this contradicts the experimental evidence, so the electronic configuration of vanadium is better represented by the formula $[\text{Ar}]3d^34s^2$; the latter formula suggests that the first two ionization energies of vanadium (see sub-topic 3.2) should involve the loss of 4s electrons, so the cations V^+ and V^{2+} should have the electronic configuration of $[\text{Ar}]3d^34s^1$ and $[\text{Ar}]3d^34s^0$, respectively; these facts are consistent with the experimental data; in contrast, the formula $[\text{Ar}]4s^23d^3$ could potentially lead to a wrong conclusion that the first two electrons are lost from the 3d subshell, which would be at odds with the experiment.

For further discussion of this problem, please refer to pages 59 and 60 of the student book.

Note: the distribution of electrons in vanadium atoms and ions can be determined experimentally from magnetic measurements; please refer to sub-topics 2.2, 13.2 and A.2 for more information.



Topic 3 – Periodicity

Quick questions

Page 71

- dental amalgam releases low levels of mercury vapor that can be absorbed by the lungs; long term, high level absorption has been linked to brain and kidney damage, however, many countries have not banned the use of these fillings as the evidence is not absolute and irrefutable;
- composite fillings have improved in their strength and durability to the point where they are a viable alternative to the mercury fillings;

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- a) iodine monobromide, IBr: iodine has 7 valence electrons and will be part of an ABE_3 system when bonding to a bromine atom; it forms a trigonal bipyramidal molecular geometry, with single I—Br sigma bond; to predict the I—Br bond length, we approximate that the atomic radius of iodine is greater than 117 pm by less than 17 pm (the difference between Cl and Br), the bond length of Br—I is approximately 250 pm (using the values on page 77 for the atomic radius of halogens and figure 4 on page 78 for trends in atomic radii);
- b) trichloromethane (chloroform), $CHCl_3$: this is a polar molecule with tetrahedral molecular geometry; the C—H sigma bond has a bond length of 107 pm as the atomic radius of hydrogen and carbon are 32 and 75 pm, respectively; with the chlorine being a much larger atom (atomic radius 100 pm), when compared to hydrogen, the bond length of the C—Cl bond is 175 pm;

Page 83

Group 2 elements have a fully-filled s subshell; the addition of an electron into the higher energy p subshell is not energetically favorable, resulting in the more positive electron affinity;



End of topic questions (page 91)

1. D; the d sublevel is made up of 5 orbitals, each contain a maximum of 2 electrons; a maximum number of 10 electrons is found in a d sublevel;
2. C; only silicon (Si) and tellurium (Te) are considered to be amongst the metalloids;
3. B; selenium is found in group 16 and has 6 valence electrons; in the case of p-block elements, the 1 is dropped from the group number;
4. C; the alkaline earth metals are found in group 2 of the Periodic Table;
5. C; the atomic radius generally decreases across a period as a result of increased effective nuclear charge and constant shielding;
6. C; the ionic radius of a cation is smaller compared to the corresponding atomic radius of the element; the ionic radius of an anion is larger than the corresponding atomic radius of the element; this fact eliminates alternative B; the other anions are all from group 17; the ionic radii increase down a group so the bromide ion is the largest;
7. D; when an alkali metal reacts with water, a metal hydroxide and hydrogen gas is produced in an exothermic reaction; the resulting aqueous solution is colorless;
8. B; non-metal oxides are acidic in nature; they create acidic solutions upon reacting with water:

$$\text{SO}_3(\text{l}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{H}_2\text{SO}_4(\text{aq}) \text{ sulfuric acid}$$

$$\text{P}_4\text{O}_{10}(\text{s}) + 6\text{H}_2\text{O}(\text{l}) \rightarrow 4\text{H}_3\text{PO}_4(\text{aq}) \text{ phosphoric acid}$$
9. C; within the halogens (group 17), their strength as an oxidizing agent decreases down the group; bromine will not oxidize the chloride ion; chlorine has higher reactivity than bromine and will be reduced gaining the electron; fluorine has the greatest tendency to be reduced when compared to the other halogens in group 17; chlorine will oxidize the iodide ion as it is higher in the reactivity series; iodine is a much weaker oxidizing agent than fluorine (see Data Booklet Table 24 for standard electrode potentials and refer to Topic 19);
10. B; aluminium oxide is amphoteric; it can act as both an acid and a base:
 - acting as an acid: $\text{Al}_2\text{O}_3(\text{s}) + 2\text{NaOH}(\text{aq}) + 3\text{H}_2\text{O}(\text{l}) \rightarrow 2\text{NaAl}(\text{OH})_4(\text{aq})$ sodium aluminate;
 - acting as a base: $\text{Al}_2\text{O}_3(\text{s}) + 6\text{HCl}(\text{aq}) \rightarrow 2\text{AlCl}_3(\text{aq}) + 3\text{H}_2\text{O}(\text{l})$ aluminium chloride;
11. a) atomic number/Z;
 b) across period 3: increasing number of protons/atomic number/Z/nuclear charge; (atomic) radius/size decreases/same shell/energy level/similar shielding/screening (from inner electrons);
 noble gases: do not form bonds (easily)/have a full/stable octet/shell/energy level and cannot attract more electrons;
12. a) solution becomes yellow/orange/brown/darker; chlorine is more reactive than iodine (and displaces it from solution); $2\text{KI} + \text{Cl}_2 \rightarrow 2\text{KCl} + \text{I}_2$
 b) no color change/nothing happens as fluorine is more reactive than chlorine;
13. a) K: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$
 K^+ : $1s^2 2s^2 2p^6 3s^2 3p^6$
 b) the first ionization energy of an element is the minimum energy required to remove an electron from a neutral gaseous atom in its ground-state; $\text{X}(\text{g}) \rightarrow \text{X}^+(\text{g}) + \text{e}^-$



- c) the first ionization energy of the alkali metals decreases down the group; this trend is the result of:
- atomic radius increasing down the group, making it easier for the valence electrons to be removed;
 - the shielding effect of the core electrons increasing faster than the increase in the nuclear charge, weakening the attraction between valence electrons and the nucleus;
- d) potassium-39 is made up of 19 protons, 20 neutrons and 19 electrons; the attraction between the electrons and the nucleus results in an atomic radius of 200 pm; when the atom loses its one valence electron, the resulting potassium cation has 19 protons and 18 electrons; the valence electrons are now more strongly held by the nucleus and the resulting ionic radius (138 pm) is smaller than the atomic radius;
- e) alkali metals can react vigorously when in contact with water to form a metal hydroxide; your hands have moisture on their surface and touching an alkali metal with your bare hands is hazardous.



Topic 4 – Chemical bonding and structure

Quick questions

Page 95

Boron trifluoride, BF_3 , has a trigonal planar molecular geometry and is an AB_3 system; boron has three valence electrons and forms an *incomplete* octet.

Sulfur hexafluoride (SF_6) has an extended valence of 12 in this octahedral molecular geometry compound.

Page 103

Microwaves increase the temperature of food by the flipping and rotation of water molecules resulting in the dissipation of energy ('Chemistry in the kitchen' section on page 102); the microwave energy is absorbed when the waves pass through food, so when the microwaves reach the center of food, they are weakened by this absorption and thus deliver less energy.

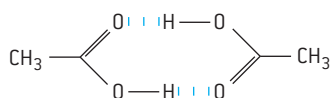
To absorb microwave energy, the molecules of water (or other polar substances) must be able to change their orientation/polarization: the H_2O molecules in the ice cannot do this very well, as both their positions and orientations are fixed; however, when the ice melts, water molecules become mobile and start absorbing microwave energy much better, so the temperature in the liquid regions increases quickly. Hence, the food close to the outside of the bowl received higher microwave flux, melts faster and once melted, absorbs microwave energy more efficiently.

Page 122

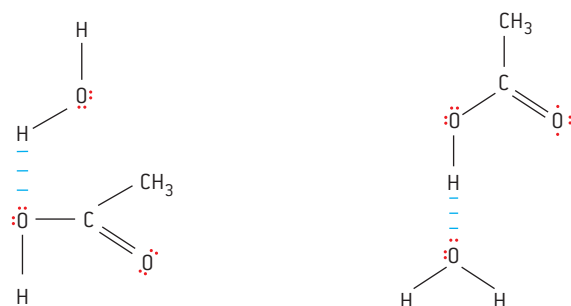
1. iodine; carbon dioxide (dry ice); naphthalene;

Page 132

An absence of water will result in carboxylic acids forming dimers, as shown:



When water is present, hydrogen bonds will form between the carboxylic acid and water; these can occur between the oxygen atom on the hydroxyl group of ethanoic acid and a hydrogen atom on water (as shown below, left) or between the hydrogen of the hydroxyl group of ethanoic acid and the oxygen atom in water (below, right).





End of topic questions (page 137)

1. C;
2. A; a magnesium atom will lose its two valence electrons to form the Mg^{2+} ion and adopt the [Ne] noble gas core; magnesium is oxidized in the process; an oxygen atom will gain two electrons to form the O^{2-} ion and adopt the [Ne] noble gas core; oxygen is reduced in the process; the ionic compound of MgO is formed;
3. B; a sodium atom will lose one valence electron to form the Na^+ ion and adopt the [Ne] noble gas core; the nitrate ion (NO_3^-) is a polyatomic ion with a single negative charge;
4. D; both sodium oxide and potassium bromide are ionic compounds; the ammonium ion and nitrate ion are polyatomic ions. Polyatomic ions are composed of two or more atoms covalently bonded together; the bonding between these two polyatomic ions is ionic; dinitrogen tetroxide is a simple molecular compound with covalent bonding between the atoms;
5. D; a carbon–oxygen covalent single bond has a longer bond length when compared to the carbon–oxygen covalent double bond; the carbon–oxygen covalent triple bond has the shortest bond length; both ethanol $\text{CH}_3\text{CH}_2\text{OH}$ and methoxymethane $(\text{CH}_3)_2\text{O}$ have carbon–oxygen covalent single bond; 2-propanone has a carbon–oxygen covalent double bond and carbon monoxide has a carbon–oxygen covalent triple bond;
6. B; the most polar bond is that with the greatest difference in electronegativity value;

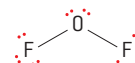
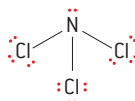
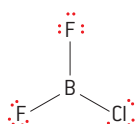
	$\Delta\chi_p$
C–H	0.4
O–H	1.2
H–Cl	1.0
C–O	0.8

7. C; phosphorus is found in group 15 and has five valence electrons; with three bonded atoms and one lone pair of electrons, VSEPR theory predicts that the AB_3E system will have 4 electron domains with a tetrahedral geometry, and a molecular geometry of trigonal pyramidal due to the repulsive effects of the lone pair of electrons; the bond angle will be less than 109.5° as a result of the LP/BP repulsion;
8. C; C_{60} or fullerene is a molecular structure consisting of 60 carbon atoms arranged in a spherical structure like a soccer ball;
9. B; the compound difluoromethane has four electron domains and a tetrahedral molecular geometry; as it contains both C–H and C–F bonds, the combination of the geometry of the polar bonds results in the molecule being polar; the dipole moments do not cancel one another out; as the molecule does not contain an H–F bond, hydrogen bonding is not present; both London forces and dipole-dipole forces are present;
10. B; the structure of a metal is a regular giant lattice that consists of positive ions (cations) surrounded by a “sea” of delocalized electrons;

11. a)

	$\text{BF}_2\text{Cl}(\text{AB}_3)$	$\text{NCl}_3(\text{AB}_3\text{E})$	$\text{OF}_2(\text{AB}_2\text{E}_2)$
(i)	Trigonal planar	Tetrahedral	Tetrahedral
(ii)	Trigonal planar	Trigonal pyramidal	V-shaped
(iii)	120°	$< 109.5^\circ$ (107°)	$< 109.5^\circ$ (104.5°)
(iv)	Polar	Polar	Polar

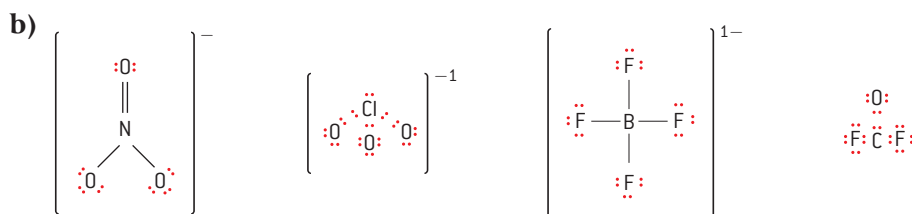
b)





12. a)

	$[\text{NO}_3]^- (\text{AB}_3)$	$[\text{ClO}_3]^- (\text{AB}_3\text{E})$	$[\text{BF}_4]^- (\text{AB}_4)$	$\text{COF}_2 (\text{AB}_3)$
(i)	Trigonal planar	Tetrahedral	Tetrahedral	Trigonal planar
(ii)	Trigonal planar	Trigonal pyramidal	Tetrahedral	Trigonal planar
(iii)	120°	$< 109.5^\circ (107^\circ)$	109.5°	120°



13. Ar: London forces only

$\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$: London + dipole – dipole + hydrogen bonding (O–H bond is present)

CH_3Cl : London + dipole – dipole

$\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$: London + dipole – dipole

14. $\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$: no hydrogen bonding

NH_3 : hydrogen bonding (N–H bond is present)

C_2H_4 : no hydrogen bonding

PH_3 : no hydrogen bonding

15.

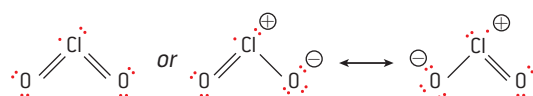
	Diamond	Graphite	Graphene	C_{60}
Structure	Covalent network solid	Covalent network solid	Covalent network solid	Molecular
Bonding	Covalent bonding	Covalent bonding	Covalent bonding	Covalent bonding
Intermolecular forces	None	London Forces	None	London Forces
Melting point	Very High	High	High	Very low
Electrical conductivity	Non conductor	Poor	Very high	Non conductor

16. **Suggest** – Propose a solution, hypothesis or other possible answer. [Assessment Objective 3]

Discuss – Offer a considered and balanced review that includes a range of arguments, factors or hypotheses. Opinions or conclusions should be presented clearly and supported by appropriate evidence. [Assessment Objective 3]

a) the term “macromolecular” is used by IUPAC primarily for polymers; each molecule of a typical polymer consists of many repeating units, and each unit contains several atoms; in covalent network solids, such as graphite, the repeating units cannot be identified (unless we allow each unit to be a single atom), so these solids are not macromolecular compounds;

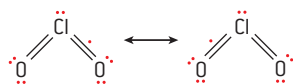
b) chlorine dioxide can be represented by several Lewis structures (see note below), for example:



In all these structures, the Cl atom has four electron domains, two of which are occupied by non-bonding electrons (one lone pair and one unpaired electron); due to increased repulsion of non-bonding electrons, the predicted bond angle O–Cl–O should be less than 109.5° while the actual angle is 110.9° ; therefore, the prediction of VSEPR theory seems to be incorrect;



Note: none of the above structures adequately represent the bonding in the ClO_2 molecule; this issue can be resolved by introducing the concept of a *three-electron bond*, which has a bond order of 0.5; a three-electron bond is often shown by a line (two electrons) and a dot (the third electron):



In these resonance structures, the Cl atom has three electron domains, one of which is occupied by a lone electron pair; according to this model, the predicted bond angle (less than 120°) is in good agreement with the experimental value (110.9°);

17. Suggest – Propose a solution, hypothesis or other possible answer. [Assessment Objective 3]

The VSEPR theory assumes that the mutual repulsion between *all* valence electrons determines the shape of the molecule; this is generally true for all bonding electrons and also for the non-bonding electrons occupying sp -, sp^2 - and sp^3 -hybrid orbitals; however, the non-bonding electrons in d-subshells can occupy highly symmetrical orbitals and produce nearly spherical distribution of electrical charge; such electrons are said to be *stereochemically inactive*, as they repel all other electrons equally in all directions (i.e., regardless of their orientation).

Many complexes of transition elements contain ions with partly filled d-subshells, so some (or all) their d-electrons can be stereochemically inactive and thus do not affect the overall shape of the ion; this is the case for $[\text{FeCl}_4]^{2-}$, which is tetrahedral despite the fact that the central atom (Fe^{+2}) in this complex formally has four non-bonding d-electrons.

In the case of $[\text{MnO}_4]^-$, the central atom (Mn^{+7}) has an empty d-subshell and thus no non-bonding d-electrons; the absence of stereochemically inactive electrons in tetrahedral $[\text{MnO}_4]^-$ and some other complex ions of transition elements allows the VSEPR theory to predict their shapes correctly.



Topic 5 – Energetics and thermochemistry

Quick questions

Page 145

- | | |
|---|---|
| a) $3\text{C(s)} + 4\text{H}_2\text{(g)} \rightarrow \text{C}_3\text{H}_8\text{(g)}$ | $\Delta H_f^\ominus = -105 \text{ kJ mol}^{-1}$ |
| b) $\text{C(s)} + \frac{3}{2}\text{H}_2\text{(g)} + \frac{1}{2}\text{Cl}_2\text{(g)} \rightarrow \text{CH}_3\text{Cl(g)}$ | $\Delta H_f^\ominus = -82 \text{ kJ mol}^{-1}$ |
| c) $2\text{C(s)} + 3\text{H}_2\text{(g)} + \frac{1}{2}\text{O}_2\text{(g)} \rightarrow \text{C}_2\text{H}_5\text{OH(l)}$ | $\Delta H_f^\ominus = -278 \text{ kJ mol}^{-1}$ |
| d) $7\text{C(s)} + 3\text{H}_2\text{(g)} + \text{O}_2\text{(g)} \rightarrow \text{C}_6\text{H}_5\text{COOH(s)}$ | $\Delta H_f^\ominus = -385 \text{ kJ mol}^{-1}$ |
| e) $\text{C(s)} + \frac{1}{2}\text{O}_2\text{(g)} \rightarrow \text{CO(g)}$ | $\Delta H_f^\ominus = -110.5 \text{ kJ mol}^{-1}$ |
| f) $\text{C(s)} + \frac{5}{2}\text{H}_2\text{(g)} + \frac{1}{2}\text{N}_2\text{(g)} \rightarrow \text{CH}_3\text{NH}_2\text{(g)}$ | $\Delta H_f^\ominus = -23 \text{ kJ mol}^{-1}$ |

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- | | |
|--|--|
| a) $\text{C}_8\text{H}_{18}\text{(l)} + \frac{25}{2}\text{O}_2\text{(g)} \rightarrow 8\text{CO}_2\text{(g)} + 9\text{H}_2\text{O(g)}$ | $\Delta H_c^\ominus = -5470 \text{ kJ mol}^{-1}$ |
| b) $\text{C}_2\text{H}_5\text{Cl(g)} + 5\text{O}_2\text{(g)} \rightarrow 2\text{CO}_2\text{(g)} + 4\text{H}_2\text{O(g)}$ | $\Delta H_c^\ominus = -1413 \text{ kJ mol}^{-1}$ |
| c) $\text{C}_6\text{H}_{12}\text{O(s)} + \frac{17}{2}\text{O}_2\text{(g)} \rightarrow 6\text{CO}_2\text{(g)} + 6\text{H}_2\text{O(g)}$ | $\Delta H_c^\ominus = -3728 \text{ kJ mol}^{-1}$ |
| d) $\text{CH}_2\text{O}_2\text{(l)} + \frac{1}{2}\text{O}_2\text{(g)} \rightarrow \text{CO}_2\text{(g)} + \text{H}_2\text{O(g)}$ | $\Delta H_c^\ominus = -255 \text{ kJ mol}^{-1}$ |
| e) $\text{C}_6\text{H}_{12}\text{O}_6\text{(s)} + 6\text{O}_2\text{(g)} \rightarrow 6\text{CO}_2\text{(g)} + 6\text{H}_2\text{O(g)}$ | $\Delta H_c^\ominus = -2803 \text{ kJ mol}^{-1}$ |

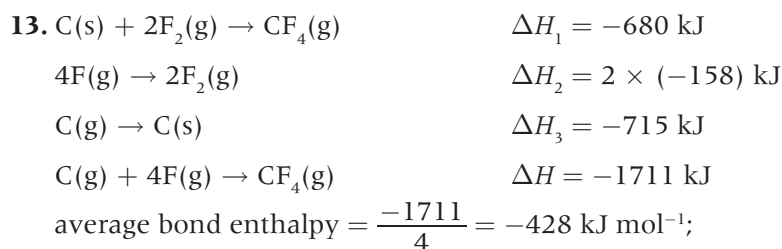
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1. bond enthalpy for H-Cl is $431.5 \text{ kJ mol}^{-1}$
2.
 - a) $\text{CH}_4\text{(g)} + \text{Cl}_2\text{(g)} \rightarrow \text{CH}_3\text{Cl(g)} + \text{HCl(g)}$
 - b) $1898 - 1997 = -99 \text{ kJ}$
 - c) exothermic
 - d) products



End of topic questions (page 157)

1. C
2. A
3. C
4. C
5. a) $2706 - 2830 = -124 \text{ kJ}$
 b) $2582 - 2380 = 202 \text{ kJ}$ (NB $\text{C}\equiv\text{O} = 1072 \text{ kJ mol}^{-1}$)
6. a) the enthalpy change when one mole of compound is formed from its elements in their standard state at standard conditions of $298 \text{ K}/25^\circ\text{C}$ and $101\,325 \text{ Pa}/1 \text{ atm}$
 b) (i) $\Delta H_p = 4 \times (-242) + 4 \times (-394) \text{ kJ mol}^{-1}$
 $\Delta H_R = 1 \text{ kJ mol}^{-1}$
 $\Delta H^\ominus = (\sum \Delta H_p^\ominus - \sum \Delta H_R^\ominus) = -2545 - (-2.55 \times 10^3) = -2550 \text{ kJ mol}^{-1}$
 (ii) products more stable than reactants; bonds are stronger in products than reactants/
 $H_p < H_R$ /enthalpy/stored energy of products less than reactants;
 (iii) same/equal, because the same bonds are being broken and formed
7. D
8. $\text{C}_2\text{H}_6(\text{g}) + 3\frac{1}{2}\text{O}_2(\text{g}) \rightarrow 2\text{CO}_2(\text{g}) + 3\text{H}_2\text{O}(\text{l}) \quad \Delta H^\ominus = -1560 \text{ kJ}$
 $\text{H}_2\text{O}(\text{l}) \rightarrow \text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \quad \Delta H^\ominus = +286 \text{ kJ}$
 $2\text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l}) \rightarrow \text{C}_2\text{H}_4(\text{g}) + 3\text{O}_2(\text{g}) \quad \Delta H^\ominus = +1411 \text{ kJ}$
 $\text{C}_2\text{H}_6(\text{g}) \rightarrow \text{C}_2\text{H}_4(\text{g}) + \text{H}_2(\text{g}) \quad \Delta H^\ominus = +137 \text{ kJ}$
9. A
10. a) $\text{C}_2\text{H}_4(\text{g}) + \text{H}_2(\text{g}) \rightarrow \text{C}_2\text{H}_6(\text{g})$
 b) products more stable than reactants/reactants less stable than products; products lower in energy; reactants higher in energy;
 c) (overall) bonds in reactants weaker and (overall) bonds in product stronger; all bonds in product are σ bonds; weaker π bond broken and a (stronger) σ bond formed; less energy needed to break weaker bonds/more energy produced to make stronger bonds (thus reaction is exothermic);
or
 bond breaking is endothermic (requires energy) and bond making is exothermic (releases energy); stronger bonds in product mean process is exothermic overall;
11. a) standard enthalpy (change) of reaction; temperature increase; reaction is exothermic; sign of $\Delta H^\ominus$ is negative;
 b) more negative; heat given out when gas changes to solid; solid has less enthalpy than gas;
 c) -389 kJ
12. a) amount of energy required to break bonds of reactants:
 $8 \times 412 + 2 \times 348 + 612 + 6 \times 496 = 7580 \text{ kJ mol}^{-1}$
 amount of energy released during bond formation:
 $4 \times 2 \times 743 + 4 \times 2 \times 463 = 9648 \text{ kJ mol}^{-1}$
 $\Delta H = -2068 \text{ kJ or kJ mol}^{-1}$
 b) exothermic and $\Delta H^\ominus$ is negative; energy is released;



14. a) amount of energy required to break bonds of reactants:

$$3 \times 413 + 358 + 464 + 1.5 \times 498 = 2808 \text{ kJ mol}^{-1}$$

amount of energy released during bond formation of products:

$$4 \times 464 + 2 \times 746 = 3348 \text{ kJ mol}^{-1}$$

$$\Delta H = -540 \text{ kJ mol}^{-1}$$

b) (i) $m(\text{methanol}) = 80.557 - 80.034 = 0.523 \text{ g}$

$$n(\text{methanol}) = \frac{0.523 \text{ g}}{32.05 \text{ g mol}^{-1}} = 0.0163 \text{ mol}$$

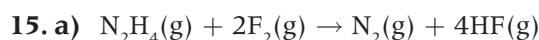
(ii) $\Delta T = 26.4 - 21.5 = 4.9 \text{ K}$;

$$q = mc\Delta T = 20.000 \times 4.18 \times 4.9 \text{ J} = 20.000 \times 4.18 \times 4.9 \times 10^{-3} \text{ kJ} = 0.41 \text{ kJ}$$

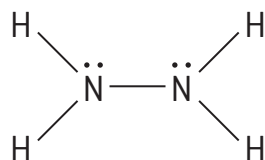
$$\text{(iii)} \quad \Delta H_c^\ominus = -\frac{0.41 \text{ (kJ)}}{0.0163 \text{ (mol)}} = -25153 \text{ J mol}^{-1} = -25 \text{ kJ mol}^{-1}$$

c) (i) bond enthalpies are average values/differ (slightly) from one compound to another (depending on the neighbouring atoms); methanol is liquid, not a gas in the reaction;

(ii) not all heat produced transferred to water; heat lost to surroundings/environment ; incomplete combustion (of methanol); water forms as $\text{H}_2\text{O(l)}$ instead of $\text{H}_2\text{O(g)}$;



b) Hydrazine:



Nitrogen:



c) amount of energy required to break bonds of reactants:

$$4 \times 391 + 158 + 2 \times 158 = 2038 \text{ kJ}$$

amount of energy released during bond formation of products:

$$945 + 4 \times 568 = 3217 \text{ kJ}$$

$$\Delta H^\ominus = 2038 - 3217 = -1179 \text{ kJ}$$

d) $(\text{N}_2\text{H}_4/\text{F}_2)$ is a better rocket fuel; 5 vol/mol (g) > 3 vol/mol (g); more moles/greater amount of gas produced; $\Delta H^\ominus (\text{N}_2\text{H}_4/\text{F}_2) > \Delta H^\ominus (\text{N}_2\text{H}_4/\text{O}_2)$ (per mole); $(\text{N}_2\text{H}_4/\text{F}_2)$ reaction more exothermic;

16. a) energy required = $\text{C}=\text{C} + \text{H}-\text{H} = 612 + 436$

$$\text{energy released} = \text{C}-\text{C} + 2(\text{C}-\text{H}) = 347 + 2 \times 413$$

$$\text{energy required} = \text{C}=\text{C} + \text{H}-\text{H} + 4(\text{C}-\text{H}) = 612 + 436 + 4 \times 413$$

$$\text{energy released} = \text{C}-\text{C} + 6(\text{C}-\text{H}) = 347 + 6 \times 413$$

$$\Delta H = (1048 - 1173) = (2700 - 2825) = -125 \text{ kJ mol}^{-1}$$



- b) $\Delta H = -1411 + (-286) - (-1560) = -137 \text{ kJ mol}^{-1}$
- c) the actual values for the specific bonds may be different to the average values; the combustion values referred to the specific compounds;
- d) (i) -125 kJ mol^{-1}
- (ii) average bond enthalpies do not apply to the liquid state; the enthalpy of vaporization/condensation of cyclohexene and cyclohexane.



Topic 6 – Chemical kinetics

End of topic questions (page 177)

1. A; for a chemical reaction to occur between two reactant particles, a number of conditions must be fulfilled:
 - the two particles must collide with each other, that is, there must be physical contact;
 - the colliding particles must have the correct mutual orientations;
 - the reactant particles must have sufficient kinetic energy to initiate the reaction;
 Examining the alternatives, only A is plausible and is related to the third condition stated above.
2. C; checking the stoichiometry, 0.21 moles of Mg are reacting with 0.2 mol of HNO_3 ; referring to the balanced equation, it is determined that the HNO_3 is the limiting reagent; to achieve the same initial reaction rate, you will require the same number of mol of HNO_3 ;
3. D; the rate of reaction is defined as the change in concentration of reactants or products per unit time;
4. C; as calcium carbonate is in excess, it is the concentration and number of mol of HCl that will influence the initial rate of reaction; curves I and II demonstrate the fastest initial rates and produce twice the volume of carbon dioxide compared to curves III and IV; the reaction conditions in columns 1 and 2 both have 0.05 mol of HCl; however, column 1 has a smaller volume within which the reaction is taking place; this increases the probability of successful collisions; column 3 has half the number of mol of HCl when compared to columns 1 and 2; it is not possible to determine if column 3 represents curves III or IV; column 1 represents curve I and column 2 represents curve II;
5. B; in a heterogeneous reaction involving a gas (or a liquid) and a solid, the rate of reaction will increase if the surface area of the solid is increased by breaking the solid up into smaller pieces; the reason for this is that the reaction takes place only on the surface of the solid reactant; if a finely divided solid or powder is used, there will be an increase in the surface area and there will be a greater number of solid particles available for reaction; this will result in greater collision frequency; increasing the surface area of the solid reactant will not alter the activation energy of the reaction;
6. A; there are four factors that can increase the rate of a chemical reaction:
 - (i) increasing the temperature at which the reaction is conducted;
 - (ii) addition of a catalyst;
 - (iii) increasing the concentration of the reactants;
 - (iv) decreasing the particle size of reactants in the solid phase;
7. D; statement I: $\text{average rate} = \frac{\Delta C}{\Delta t} = \frac{1.50 - 0.35 \text{ mol dm}^{-3}}{3.5 \text{ min}} = 0.33 \text{ mol dm}^{-3} \text{ min}$; statement II: with increasing temperature, the frequency of collisions will increase; there will be more successful collisions, since there are now more particles which have sufficient kinetic energy to overcome the activation energy barrier; statement III: esterification is a reversible reaction that occurs when a carboxylic acid and an alcohol are heated in the presence of a catalyst, normally concentrated sulfuric acid; acid – catalyzed hydrolysis is the reverse of esterification and results in the formation of a carboxylic acid and an alcohol;
8. (i) increase in concentration of product per unit time/decrease in concentration of reactant per unit time;
 - (ii) frequency of collisions; kinetic energy/speed of reactant particles; collision geometry/orientation;



9. a) (i) increases rate of reaction; molecules (of H_2O_2) collide more frequently/more collisions per unit time;
- (ii) no effect/(solution) remains unchanged; solid NaI is not reacting/aqueous solution of NaI is reacting/surface area of NaI is not relevant in preparing the solution;
- b) kinetic energy/speed of reacting molecules increases; frequency of collisions increases per unit time; greater proportion of molecules have energy greater than activation energy/ E_a ;

10. **Discuss** – Offer a considered and balanced review that includes a range of arguments, factors or hypotheses. Opinions or conclusions should be presented clearly and supported by appropriate evidence. [Assessment Objective 3]

NOS 1.10. Models, some simple, some very complex, based on theoretical understanding, are developed to explain processes that may not be observable; computer-based mathematical models are used to make testable predictions, which can be especially useful when experimentation is not possible; models tested against experiments or data from observations may prove inadequate, in which case they may be modified or replaced by new models.

In the kinetic-molecular theory of gases, a sample of gas is modelled as consisting of a collection of particles moving at high velocities in random directions; the sizes of the particles are negligible; the particles collide with each other and with the walls of the container containing the gaseous sample; all the collisions are elastic; the pressure exerted by the gas results from collisions of its particles with the walls of the container; the three conditions that form the basis of collision theory are given in answer to question 1 above; the collision theory is a model that helps us understand why rates of chemical reactions depend on temperature; the model is based on the kinetic-molecular theory.

11. To design an appropriate experiment to measure the rate of reaction of a hydrolysis reaction (saponification) of the ester methyl ethanoate in an alkaline medium, we must first examine the chemical reaction ($\text{CH}_3\text{COOCH}_2\text{CH}_3 + \text{NaOH} \rightarrow \text{CH}_3\text{COONa} + \text{CH}_3\text{CH}_2\text{OH}$), which is second order as the rate of saponification is directly proportional to the concentration of the ester and the alkali; while the reaction proceeds, samples from the reaction mixture are taken periodically and analyzed using gas chromatography (GC), high performance liquid chromatography (HPLC), nuclear magnetic resonance (NMR), infrared spectroscopy (IR) or even mass spectroscopy (MS):

- GC will show individual peaks of all volatiles, including methanol, ethanoic acid and methyl ethanoate; these peaks can be individually integrated, and exact amounts/concentrations of all substances can be calculated using a calibration curve (made from standard samples of methanol, ethanoic acid and ester);
- HPLC will be very similar to GC;
- NMR will be problematic, but still possible, as the signals of CH_3 groups in CH_3OH , CH_3COOH and $\text{CH}_3\text{C}(\text{O})\text{OCH}_3$ will all have slightly different chemical shifts (please note that we cannot look at OH groups, as the medium is aqueous, and all OH peaks will be too broad to detect);
- IR will show slightly different absorptions for the $\text{C}=\text{O}$ groups in the acid and ester, and also very different absorptions in the fingerprint region; we will not be able to interpret those directly, but if we prepare a series of standard solutions containing known mixtures of CH_3OH , CH_3COOH and $\text{CH}_3\text{C}(\text{O})\text{OCH}_3$, we'll be able to build a calibration curve or just match the spectra of the reaction mixture to the nearest standard;
- MS will be unclear unless we are using chemical ionization instead of electron impact, but similar to IR, it will be possible to interpret it using a calibration curve or just a series of standards;

When neither one of these techniques is available, we can still take samples of the reaction mixture and titrate with ethanoic acid; the saponification of the ester will partially consume the base [for example, $\text{CH}_3\text{C}(\text{O})\text{OCH}_3 + \text{KOH} \rightarrow \text{CH}_3\text{COOK} + \text{CH}_3\text{OH}$]; the concentration of the remaining base can be compared with the initial concentration of this base, and the extent of the saponification calculated; the key here is to use the same acid (ethanoic) as the titrant, because if we use a strong acid, it will also react with both KOH and CH_3COOK , and thus will show about the same result



regardless of the saponification extent, but also to use the correct indicator (phenolphthalein with pK_a 9.6 is the best), as the pH at the equivalence point will be greater than 7 (because CH_3COOK is a salt of a weak acid and a strong base); finally, if possible, use a colorimeter; the accuracy and precision of the experiment can be improved by taking multiple measurements, using different students and also by preparing standards with known concentrations of CH_3OH , CH_3COOH , $\text{CH}_3\text{C}(\text{O})\text{OCH}_3$ and KOH (we have to titrate these standards as well and build a calibration curve showing the known concentration of KOH against the concentration of KOH determined by our titration – this will eliminate or reduce most systematic errors);

12. At the beginning of the reaction of Mg with dilute HCl , the addition an acid-base indicator will result in a color change when a certain percentage of HCl is consumed; from the *IB Data Booklet*, the most suitable indicators are methyl orange (pK_a 3.7, red to yellow), bromophenol blue (pK_a 4.2, yellow to blue), bromocresol green (pK_a 4.7, yellow to blue) and methyl red (pK_a 5.1), as other indicators will change color at too high a pH, which will not be achieved within a reasonable time during this reaction; the observed color of the reaction mixture will be accurate if a standard is used; start the experiment by preparing a buffer solution of $\text{pH} = 4.0$, add exactly the same amount of indicator to the flask and place both flasks (with HCl/Mg and standard) side by side on a white sheet of paper; when the colors of both flasks are the same, stop the timer and record the result; to eliminate random errors, repeat the experiment three times; to reduce systematic errors, ask different students to look at the color (as individual perceptions can vary).



Topic 7 - Equilibrium

Quick questions

Page 182

C

Page 183

- a) $K_c = \frac{[\text{NH}_3]}{[\text{N}_2]^{1/2}[\text{H}_2]^{3/2}}$
- b) $K_c = \frac{[\text{NO}_2][\text{ClNO}]}{[\text{ClNO}_2][\text{NO}]}$
- c) $K_c = \frac{[\text{NO}]^4[\text{H}_2\text{O}]^6}{[\text{O}_2]^5[\text{NH}_3]^4}$

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1. $\frac{1}{K_c} = 4.2 \times 10^{-34}$
2. $\sqrt{K_c} = 0.028$

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- a) the reaction is endothermic; an increase in the temperature of the system will shift the equilibrium, favoring the forward reaction, increasing the volume of PCl_3 and Cl_2 ;
- b) as chlorine gas is a product, an increase in the volume of chlorine will shift the equilibrium, favoring the reverse reaction;
- c) in this system, there is 1 mol of gas on the reactant side and 2 mol of gas on the product side; an increase in pressure will shift the equilibrium to favor the side with the least number of moles of gas, the reactant side;
- d) the addition of a catalyst increases the rate of the forward and reverse reactions equally; there is no shift in the equilibrium position;

End of topic questions (page 190)

1. D
2. D
3. D

4. a) $K_c = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]}$

horizontal line: concentration of reactant and product remains constant/equilibrium reached; magnitude of K_c greater than 1; product concentration greater than reactant concentration;

- b) increased temperature shifts equilibrium position to right; (forward) reaction is endothermic/absorbs heat;
- c) increased pressure shifts equilibrium to left; fewer (gas) moles/molecules on left;
- d) both/forward and reverse rates increased/increase in forward reverse rates are equal; activation energy reduced; position of equilibrium unchanged; concentration/amount of reactants and products remain constant; value of K_c unchanged; K_c only affected by changes in temperature;



Topic 8 – Acids and bases

Quick questions (page 194)

1. a) HSO_4^- b) NO_3^- c) $\text{C}_2\text{H}_5\text{O}$ d) $\text{C}_6\text{H}_5\text{O}^-$ e) O^{2-} f) OH^-
 2. a) H_2O b) H_3O^+ c) NH_4^+ d) HCO_3^- e) H_2NO_3^+ f) $\text{C}_2\text{H}_5\text{NH}_3^+$

3.

	conjugate acid 1	conjugate base 1	conjugate base 2	conjugate acid 2
Reaction 1	HCO_3^-	CO_3^{2-}	S^{2-}	HS^-
Reaction 2	CH_3COOH	CH_3COO^-	HPO_4^{2-}	H_2PO_4^-

End of topic questions (page 207)

- C
- C
- D
- water can act as a Brønsted-Lowry acid by donating a proton/ H^+ to form OH^- ;
water can act as a Brønsted-Lowry base by accepting a proton/ H^+ to form H_3O^+ ;
- B
- B
- C
- C
- C
- black coffee;
 10^3 or 1000 times;
- $n(\text{HCl}) = (0.100 \times 0.50) = 0.050 \text{ mol}$
 $n(\text{NaOH}) = (0.200 \times 0.10) = 0.020 \text{ mol}$
 $n(\text{HCl})_{\text{remaining}} = (0.050 - 0.020) = 0.030 \text{ mol}$
- A
- C
- D
- a)
- (measuring) the pH: the strong acid solution will have a lower pH; conductivity (measurement): the strong acid will be a better conductor; the strong acid will react more vigorously with metals/carbonates; the heat change when it is neutralized with a base will be different; heat of neutralization;
- a) partially dissociated or ionized;
 $\text{CH}_3\text{COOH} + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{COO}^- + \text{H}_3\text{O}^+ / \text{CH}_3\text{COOH} \rightleftharpoons \text{CH}_3\text{COO}^- + \text{H}^+$
b) $2\text{CH}_3\text{COOH} + \text{CaCO}_3 \rightarrow \text{Ca}(\text{CH}_3\text{COO})_2 + \text{CO}_2 + \text{H}_2\text{O}$
- a) acid in both reactions; because it loses a proton/hydrogen ion/ H^+ or is a proton/hydrogen ion/ H^+ donor;
b) NH_2^- more readily accepts a proton; equilibrium lies to the right; takes H^+ from H_2O ;
c) NH_4^+ ; donates a proton more readily than NH_3 ; equilibrium lies to the left.



Topic 9 – Redox processes

Quick questions

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1. a) +4 b) +7 c) +5 d) 0
 e) -3 (the oxidation state of hydrogen is assumed to be +1 when it is bonded to a non-metal, even when the non-metal (in our case, phosphorus) has the same electronegativity as hydrogen)
 f) +1 g) +3 h) +3 i) +5
2. a) Cl^0 in Cl_2 , I^{-1} in KI , Cl^{-1} in KCl and I^0 in I_2
 b) iodine is oxidized (from -1 to 0) and chlorine is reduced (from 0 to -1)
 c) $\text{Cl}_2(\text{aq})$ is the oxidizing agent and $\text{KI}(\text{aq})$, or, more precisely, $\text{I}^{-}(\text{aq})$, is the reducing agent

Page 219

1. $2\text{KBr} + \text{Cl}_2 \rightarrow 2\text{KCl} + \text{Br}_2$ (the states can vary);
 Cl_2 is the oxidizing agent and KBr is the reducing agent.

Halogen	$\text{Cl}_2(\text{aq})$	$\text{Br}_2(\text{aq})$
a) Reaction with $\text{KI}(\text{aq})$	Yes	Yes
b) Colour of halide solution	Yellow to brown*	Yellow to brown*
c) Balanced equation	$2\text{KI}(\text{aq}) + \text{Cl}_2(\text{aq}) \rightarrow 2\text{KCl}(\text{aq}) + \text{I}_2(\text{aq})$ or $3\text{KI}(\text{aq}) + \text{Cl}_2(\text{aq}) \rightarrow 2\text{KCl}(\text{aq}) + \text{KI}_3(\text{aq})$	$2\text{KI}(\text{aq}) + \text{Br}_2(\text{aq}) \rightarrow 2\text{KBr}(\text{aq}) + \text{I}_2(\text{aq})$ or $3\text{KI}(\text{aq}) + \text{Br}_2(\text{aq}) \rightarrow 2\text{KBr}(\text{aq}) + \text{KI}_3(\text{aq})$

* depending on the reaction conditions, aqueous iodine (yellow) or aqueous triiodide ions (yellow to brown) can form in this reaction; equations involving triiodides are discussed only in Options (see Chapters B.4 and C.8) and are therefore not required for Papers 1 and 2.

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- a) $\text{Zn}(\text{s})|\text{Zn}^{2+}(\text{aq})||\text{Fe}^{2+}(\text{aq})|\text{Fe}(\text{s})$
- b) cathode (positive electrode): $\text{Fe}^{2+}(\text{aq}) + 2\text{e}^{-} \rightarrow \text{Fe}(\text{s})$
 anode (negative electrode): $\text{Zn}(\text{s}) \rightarrow \text{Zn}^{2+}(\text{aq}) + 2\text{e}^{-}$
- c) potassium chloride, potassium nitrate, ammonium nitrate, etc.
- d) electrons move from the zinc electrode (anode) to the iron electrode (cathode) through the external circuit; the $\text{Zn}^{2+}(\text{aq})$ ions are formed from $\text{Zn}(\text{s})$ at the anode and move into the aqueous solution in the left hand side cell; the $\text{Fe}^{2+}(\text{aq})$ ions in the aqueous solution in the right hand side cell move towards the iron cathode and form $\text{Fe}(\text{s})$; the counter-ions (anions) move through the salt bridge from the right hand side cell to the left hand side cell;
- e) if the positive and negative ions in the salt bridge have different charges and/or sizes, they will move at different rates in the electric field; this will produce a junction potential, which will affect the potential difference generated by the voltaic cell.

Section 9 of the *IB Data Booklet* gives ionic radii only for elemental ions. While potassium chloride is the most common electrolyte for the salt bridge, the ionic radii of K^{+} (138 pm) and Cl^{-} (181 pm) are somewhat different, so $\text{KCl}(\text{aq})$ will create a noticeable junction potential in the cell; in the case of ammonium nitrate, the sizes (and thus mobilities) of NH_4^{+} and NO_3^{-} ions are closer to each other, so the junction potential of $\text{NH}_4\text{NO}_3(\text{aq})$ will be lower than that for $\text{KCl}(\text{aq})$;

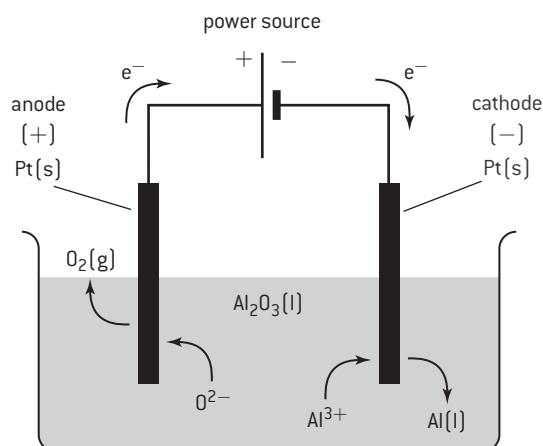
- f) it reduces the diffusion between the solutions in the salt bridge and half-cells;



Page 232

1. ions in solid lead(II) bromide cannot move freely (as their positions are fixed in the crystal lattice); a material with no free-moving electrical charges cannot conduct electricity;

2. a)



b) *cathode (negative electrode):* $\text{Al}^{3+} + 3\text{e}^- \rightarrow \text{Al(l)}$

anode (positive electrode): $2\text{O}^{2-} \rightarrow \text{O}_2(\text{g}) + 4\text{e}^-$

overall cell reaction: $4\text{Al}^{3+} + 6\text{O}^{2-} \rightarrow 4\text{Al(l)} + 3\text{O}_2(\text{g})$

or



Note: the states of Al^{3+} and O^{2-} in molten Al_2O_3 are difficult to define, so they are usually omitted

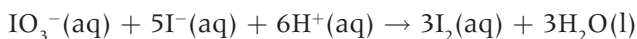
- c) any inert metal, such as platinum; in the industry, graphite electrodes are used (see Chapter A.2 for more information);
- d) electrons move from the anode (positive electrode) to the cathode (negative electrode) through the external circuit; the Al^{3+} ions from molten Al_2O_3 move to the cathode and form Al(l) ; the O^{2-} ions from molten Al_2O_3 move to the anode and form $\text{O}_2(\text{g})$;
- e) at the cathode (negative electrode), liquid aluminium forms (and flows down to the bottom of the electrolytic cell, as the density of aluminium is higher than that of aluminium oxide); at the anode, bubbles of oxygen gas form (and escape to the atmosphere);
- f) the discussion may include the following:
 - the density of aluminium is lower than that of iron while the strength of aluminium (especially when it is alloyed with other elements) is sufficient for most applications, so an object or construction made of aluminium can be almost as strong as that of iron or steel but weigh less;
 - in contrast to iron, a thin film of aluminium oxide protects the bulk of the metal from further oxidation, so aluminium does not need to be painted or otherwise protected from corrosion;
 - the melting point of aluminium is lower than that of iron, so aluminium is easier to shape by moulding;
 - aluminium is more malleable and ductile than iron, so aluminium is easier to shape by pressing, hammering or pulling;
 - aluminium has lower electrical resistance than iron, so aluminium can be used as a construction material and, at the same time, an electrical conductor.



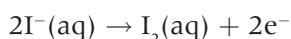
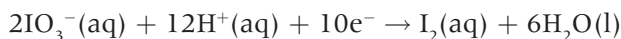
End of topic questions (page 233)

1. B; NO_3^- is the only species where the oxidation state of nitrogen (+5) is greater than that in NO_2 (+4);
2. D; metal zinc can only lose electrons (undergo oxidation), so it is the reducing agent; electrons are negatively charged, so when zinc loses electrons, the zinc electrode becomes negative;
3. C; the oxidation state of bromine in BrO_3^- is +5 and in Br_2 it is 0; when the oxidation state of an element decreases, the element undergoes reduction;
4. B; the third equation tells us that Z is more active than X (as Z can displace X); the second equation shows that Z is less active than Y (as Z cannot displace Y); the first equation is not needed for obtaining the answer, but it still confirms it (Y is more active than X);
5. C; answer A is incorrect because chlorine (yellow-green gas) is produced at the positive electrode; answer B is incorrect because sodium (silvery metal) is produced at the negative electrode; finally, answer D is incorrect because sodium ions gain electrons and thus undergo reduction:
 $\text{Na}^+ + \text{e}^- \rightarrow \text{Na(l)}$
6. A; bromine anion is the only species that loses electrons and increases its oxidation state in the course of the reaction;
7. A; both $\text{Zn}^{2+}(\text{aq})$ and $\text{Cl}_2(\text{g})$ undergo reduction, which in a voltaic cell takes place at the cathode; in contrast, Mg(s) undergoes oxidation, which takes place at the anode;
8. A; answer B is incorrect because in this cell, the salt bridge provides the flow of negative (not positive) ions; answer C is incorrect because ions cannot flow through the external circuit; similarly, answer D is incorrect because electrons cannot flow through the salt bridge;
9. this is a complex problem that requires several steps to solve:

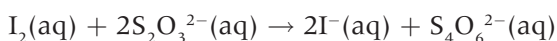
Step 1 - in acidified aqueous solutions, iodates and iodides react with each other:



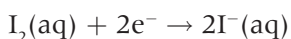
In this equation, $\text{IO}_3^-(\text{aq})$ is the oxidizing agent while $\text{I}^-(\text{aq})$ is the reducing agent:



Step 2 - the elemental iodine produced in the first equation will react with thiosulfate ions:



In this equation, $\text{I}_2(\text{aq})$ is the oxidizing agent while $\text{S}_2\text{O}_3^{2-}(\text{aq})$ is the reducing agent:

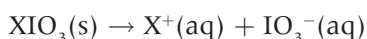


Step 3 - the molecular mass of $\text{Na}_2\text{S}_2\text{O}_3 \times 5\text{H}_2\text{O}$ is 248.22, so the sodium thiosulfate solution

contains $\frac{25.49}{248.22} \approx 0.1027 \text{ mol dm}^{-3}$ thiosulfate ions. The amount of thiosulfate ions reacted with iodine in step 2 is $0.1027 \times 0.03664 = 0.003763 \text{ mol}$, so the amount of $\text{I}_2(\text{aq})$ is $\frac{0.003763}{2} \approx$

0.001882 mol . In step 1, each iodate ion produces three molecules of iodine, so the amount of $\text{IO}_3^-(\text{aq})$ is $\frac{0.001882}{3} \approx 0.0006273 \text{ mol}$

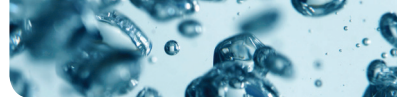
Step 4 - the amount of XIO_3 is equal to the amount of $\text{IO}_3^-(\text{aq})$:



Therefore, $n(\text{XIO}_3) = 0.0006273 \text{ mol}$ and so $M_r(\text{XIO}_3) = \frac{0.1337}{0.0006273} \approx 213.14$. Finally, $A_r(\text{X}) = 213.1 - 126.90 - 3 \times 16.00 = 38.2$. The alkali metal with the closest relative atomic mass (39.10) is K (potassium).



- 10. a)** as for most gases, the solubility of oxygen in water decreases when the temperature of water increases;
- b)** fertilizer will provide nutrients for the growth of algae and other microorganisms; these microorganisms will eventually die and undergo aerobic decay, which will consume dissolved oxygen; this process is known as eutrophication;
- 11.** Similar to the previous question, nitrates and phosphates will stimulate the growth (and, eventually, the aerobic decay) of microorganisms, causing eutrophication;
- 12. a)** each molecule of oxygen gained four moles of electrons and thus underwent reduction:
$$\text{O}_2(\text{aq}) + 2\text{H}_2\text{O}(\text{l}) + 4\text{e}^- \rightarrow 4\text{OH}^-(\text{aq})$$
- b)** from +4 in $\text{MnO}_2(\text{s})$ to +2 in $\text{Mn}^{2+}(\text{aq})$; manganese undergoes reduction;
- c)** the answer can be obtained by reversing all reaction steps: 0.0002 mol of $\text{I}^-(\text{aq}) \rightarrow 0.0001$ mol of $\text{I}_2(\text{aq}) \rightarrow 0.0001$ mol of $\text{MnO}_2(\text{s}) \rightarrow 0.00005$ mol of $\text{O}_2(\text{aq})$.



Topic 10 – Organic chemistry

Quick questions

Page 238

1. a) from the first member to the fifth member: boiling points increase; increasing size of molecule/ area of contact/number of electrons; increase in strength of intermolecular/van der Waals'/ London/dispersion forces, hence more energy required to break the intermolecular bonds;
- b) same general formula; successive members differ by CH_2 ; same functional group; similar or the same chemical properties; gradual change in physical properties;

2. a)

Isomer	A	B	C
Boiling Point	36 °C	28 °C	10 °C

increase in branching; more side chains; more spherical shape; reduced surface contact / less closely packed; weaker intermolecular force/van der Waals'/London/dispersion forces;

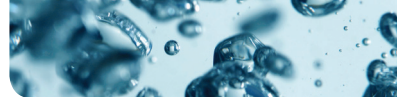
- b) B: 2-methylbutane or methylbutane;
C: 2,2-dimethyl propane or dimethyl propane;

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- a) 3-methylhexane
- b) 2,4,4-trimethylhexane
- c) 3-ethyl-2,4-dimethylhexane
- d) 3,3-dimethylpentane

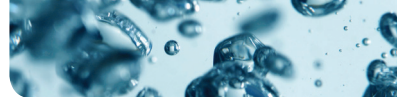
Page 249

- a) propane: $\text{C}_3\text{H}_8(\text{g}) + 5\text{O}_2(\text{g}) \rightarrow 3\text{CO}_2(\text{g}) + 4\text{H}_2\text{O}(\text{g})$
- b) pentane: $\text{C}_5\text{H}_{12}(\text{l}) + 8\text{O}_2(\text{g}) \rightarrow 5\text{CO}_2(\text{g}) + 6\text{H}_2\text{O}(\text{g})$
- c) hexane: $2\text{C}_6\text{H}_{14}(\text{l}) + 19\text{O}_2(\text{g}) \rightarrow 12\text{CO}_2(\text{g}) + 14\text{H}_2\text{O}(\text{g})$

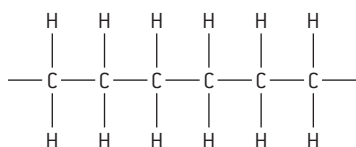


End of topic questions (page 259)

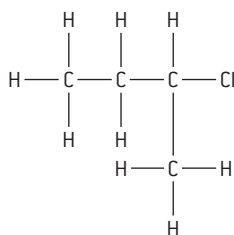
1. A
2. C
3. A
4. a) from the first member to the fifth member: boiling points increase; increasing size of molecule/area of contact/number of electrons; strength of intermolecular/van der Waals'/London/dispersion forces increase, so more energy required to break the intermolecular bonds;
 b) same general formula; successive members differ by CH_2 ; same functional group; similar or the same chemical properties; gradual change in physical properties;
5. a) colour change from yellow/orange/rust colour/red/brown to colourless;
 b) chloroethene:
$$\begin{array}{c} \text{H} & & \text{H} \\ & \diagdown & / \\ & \text{C} = \text{C} \\ & / & \diagdown \\ \text{H} & & \text{:}\ddot{\text{Cl}}\text{:} \end{array}$$
 poly(chloroethene):
$$\text{---}[\text{CH}_2\text{---CHCl}]_n\text{---}$$
- c) hydration of ethene for the manufacture of ethanol: $\text{C}_2\text{H}_4 + \text{H}_2\text{O} \rightarrow \text{C}_2\text{H}_5\text{OH}$; synthesis of CH_3COOH /ethanoic/acetic acid; synthesis of ethylene glycol/1,2-ethanediol/ethane-1,2-diol; synthesis of drugs and/or pesticides; hydrogenation of unsaturated oils in the manufacture of margarine;
6. a) primary
 b) secondary
 c) primary;
 c) / a): only one alkyl group; 2 H atoms attached to the carbon atom attached to the Cl; only one carbon atom attached to the carbon atom attached to the Cl; b): two alkyl groups; 1 H atom attached to the carbon atom attached to the Cl; two carbon atoms attached to the carbon atom attached to the Cl;
7. a) $n_c = \frac{81.7}{12.01} = 6.80$ and $n_H = \frac{18.3}{1.01} = 18.1$; ratio of 1: 2.67/1: 2.7; C_3H_8
 b) C_3H_8
 c) (i) Br_2 /bromine; UV/ultraviolet light;
 (ii) $\text{Cr}_2\text{O}_7^{2-}/\text{MnO}_4^-$ and acidified/ $\text{H}^+/\text{H}_3\text{O}^+$; heat / reflux;
- D. initiation:
 $\text{Br}_2 \rightarrow 2\text{Br}\cdot$
 propagation:
 $\text{Br}\cdot + \text{RCH}_3 \rightarrow \text{HBr} + \text{RCH}_2\cdot$
 $\text{RCH}_2\cdot + \text{Br}_2 \rightarrow \text{RCH}_2\text{Br} + \text{Br}\cdot$
 termination:
 $\text{Br}\cdot + \text{Br}\cdot \rightarrow \text{Br}_2$
 $\text{RCH}_2\cdot + \text{Br}\cdot \rightarrow \text{RCH}_2\text{Br}$
 $\text{RCH}_2\cdot + \text{RCH}_2\cdot \rightarrow \text{RCH}_2\text{CH}_2\text{R}$
8. a) A = $\text{CH}_3(\text{CH}_2)_7\text{CHO}$
 B = $\text{CH}_3(\text{CH}_2)_7\text{COOH}$
 C = $(\text{CH}_3)_3\text{COH}$
 D = $(\text{CH}_3)_2\text{CO}$
 E = $\text{BrCH}_2\text{CH}_2\text{Br}$



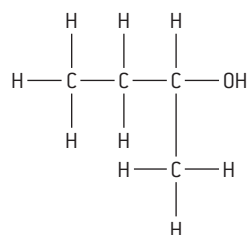
b) addition;



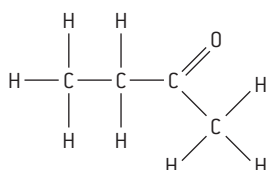
9. a)



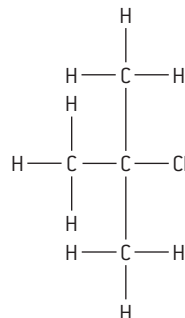
b)



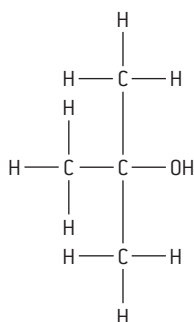
c)



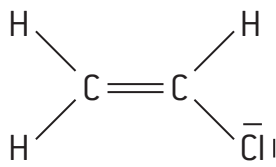
d)



e)

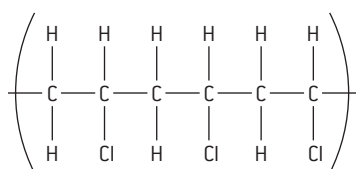


11. a)



(approximately) 120° ;

b)



c) plastics are cheap, versatile and a large industry; plastics have many uses; plastics are not biodegradable; plastics take up large amounts of space in landfill; pollution caused by burning of plastics.



Topic 11 – Measurement and data processing

End of topic questions (page 289)

1. C; note that each trailing zero is also counted as a significant figure;
2. A; answer II is incorrect, as $27.78 > 27.70 + 0.05 = 27.75$
3. C; the least precise value (3.70 cm^3) has three SF, so the answer should also be rounded to three SF;
4. C; a typical laboratory beaker has no thermal insulation; the error will be caused by the loss of heat to the environment;
5. A; in contrast to systematic errors, random errors tend to cancel one another when the experiment is repeated several times;
6. the molecular formula of codeine is $\text{C}_{18}\text{H}_{21}\text{N}_1\text{O}_3$, so $IHD = 18 - 0.5 \times 21 + 0.5 \times 1 + 1 = 9$; the same result can be obtained by counting rings and π -bonds: there are five rings, one double $\text{C}=\text{C}$ bond, and one aromatic system of six π -electrons (equivalent to three π -bonds), so $IHD = 5 + 1 + 3 = 9$
7. $IHD = 5 - 0.5 \times 10 + 0.5 \times 2 + 1 = 2$
8. a) $\text{CH}_3-\text{CH}_2-\text{CHO}$; the spectrum shows three different chemical environments of H atoms, so it cannot be $\text{CH}_3-\text{CO}-\text{CH}_3$ (it has only one chemical environment of H atoms) or $\text{CH}_2=\text{CH}-\text{CH}_2\text{OH}$ (it has four chemical environment of H atoms); also, the integration ratio of signals is 3 : 2 : 1, which is true only for $\text{CH}_3-\text{CH}_2-\text{CHO}$; finally, the signal in the 9.4–10 ppm region can belong only to the CHO group (all other signals will appear below 7 ppm);
 b) this question is somewhat incorrect, as no two signals in these compounds will have *exactly* the same chemical shift and shape; however, the signal of the CH_3 group in $\text{CH}_3-\text{CO}-\text{CH}_3$ will have approximately the same chemical shift (2.2–2.7 ppm) as the signal of the CH_2 group in $\text{CH}_3-\text{CH}_2-\text{CHO}$ (2.5 ppm), as both groups are adjacent to a carbonyl group;
 c) i) 1700–1750 cm^{-1} due to the aldehyde group (CHO);
 ii) 1620–1680 cm^{-1} due to the $\text{C}=\text{C}$ bond in $\text{CH}_2=\text{CH}-\text{CH}_2\text{OH}$ and 3200–3600 cm^{-1} due to the hydrogen bonding in alcohols (O–H bond in the same compound);
 d) $\text{C}_3\text{H}_6\text{O}^{+}$ with $\frac{m}{z} = 58$ (molecular ion), CHO^+ with $\frac{m}{z} = 29$ (loss of C_2H_5 group), $\text{C}_2\text{H}_5\text{O}^+$ with $\frac{m}{z} = 29$ (loss of CHO group), CH_3^+ with $\frac{m}{z} = 15$ (loss of CH_2CHO fragment).



Topic 12 – Atomic structure (AHL)

End of topic questions (page 300)

1. B; when solving this style of question, examine the graph or tabulated data to determine the point at which there is a rapid increase in the ionization energy; the largest jump occurs between IE_4 and IE_5 ; this corresponds to a change in energy level and therefore the element must be in Group 14;
2. C; boron is found in group 13; it will lose 3 successive valence electrons before a change in energy level takes place; therefore the greatest difference is between IE_3 and IE_4 ;
3. C; answer A is incorrect because successive ionization energy values increase, not decrease; answer B is incorrect because molar ionization energy are measured in kJ mol^{-1} ; alternative D is incorrect because ionization energy increase (not decrease) across the period as effective nuclear charge increases and atomic radii decrease;
4.
 - i) first ionization energy: $M(g) \rightarrow M^+(g) + e^-$ / the (minimum) energy (in kJ mol^{-1}) to remove one electron from a gaseous atom/the energy required to remove one mole of electrons from one mole of gaseous atoms; periodicity: repeating pattern of (physical and chemical) properties;
 - ii) evidence for main levels: highest values for noble gases/lowest values for alkali metals; general increase across a period; evidence for sub-levels: drop in I.E. from Be to B/Mg to Al/Group 2 to Group 3; drop in I.E. from N to O/P to S/Group 5 to Group 6;
 - iii) $M^+(g) \rightarrow M^{2+}(g) + e^-$

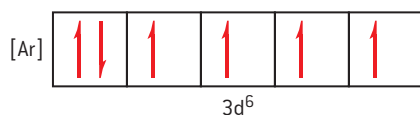


Topic 13 – The periodic table: the transition metals (AHL)

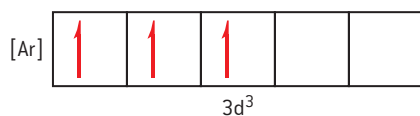
Quick questions

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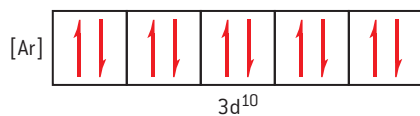
1. a) Co: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^7$
 b) Zn: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10}$; according to IUPAC, a transition element is an element that has an atom with an incomplete d-sublevel or that gives rise to cations with an incomplete d-sublevel; as zinc does not satisfy either of these conditions, it cannot be considered a transition metal;
2. a) V: $[\text{Ar}] 4s^2 3d^3$
 b) Mn: $[\text{Ar}] 4s^2 3d^5$
 c) Mn^{2+} : $[\text{Ar}] 3d^5$
3. a) Co^{3+} : $[\text{Ar}] 3d^6$



- b) Cr^{3+} : $[\text{Ar}] 3d^3$



- c) Cu^+ : $[\text{Ar}] 3d^{10}$





End of topic questions (page 327)

1. D; zinc is not considered a transition metal according to the IUPAC as it has a full d-subshell containing 10 electrons;
2. C; cobalt the element has the electronic configuration of $[\text{Ar}] 4s^2 3d^7$; it will lose 2 electrons from the highest energy orbital, in this case the 4s, creating the Co^{2+} ion: $[\text{Ar}] 3d^7$;
3. C; iron has the electronic configuration of $[\text{Ar}] 4s^2 3d^6$; when a transition element loses electrons, they are removed from the orbital of highest principle quantum number, in this case the 4s; on removal of the two electrons, the resulting electron configuration is $4s^0 3d^6$;
4. C; a ligand is an atom, molecule, or ion that contains a lone pair of electrons (non-bonding pair) that coordinates, through coordinate bonding, to a central transition metal ion to form a complex; in this complex, water acts as a ligand;
5. C;

$$\text{Na}[\text{Fe}(\text{EDTA})] \cdot 3\text{H}_2\text{O}$$

$$(+1) + x + (-4) + 3(0) = 0$$

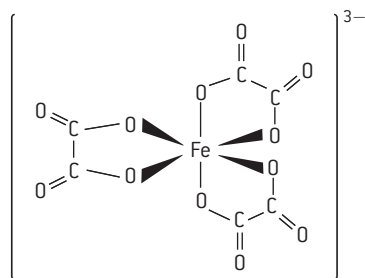
$$x = +3$$
6. C;

$$[\text{Ni}(\text{NH}_3)_6]^n$$

$$(2+) + 6(0) = 2+$$
7. D; both phosphane (PH_3) and water (H_2O) contain at least one lone pair of electron on the central atom, enabling them to act as a ligand; the nitrite ion (NO_2^-) can form coordination complexes in a number of ways;
8. D; the color of transition metal ions is associated with partially filled d orbitals; the d-to-d electronic transition is the origin of the color of transition metal complexes;
9. C; the Zn^{2+} ion does not form colored solutions as it has a full d shell and no d-to-d electronic transition are possible; both the Fe^{2+} and Co^{3+} ions have partially filled d-orbital that can experience d-to-d electronic transition;
10. A; the chromium complex has the electronic configuration of $1s^2 2s^2 2p^6 3s^2 3p^6 3d^3$; atoms with paired electrons are diamagnetic while atoms with unpaired electrons are paramagnetic; the Cr^{3+} ion has three unpaired d-electrons;
11. Ti: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^2$
 Ti^{2+} : $1s^2 2s^2 2p^6 3s^2 3p^6 3d^2$
 Ti^{3+} : $1s^2 2s^2 2p^6 3s^2 3p^6 3d^1$
 Ti^{4+} : $1s^2 2s^2 2p^6 3s^2 3p^6$
 Ca: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$
 Calcium will lose the two 4s electrons, resulting in a pseudo-noble gas configuration and a stable full outer shell; the jump from IE_2 ($1145.4 \text{ kJ mol}^{-1}$) to IE_3 ($4912.4 \text{ kJ mol}^{-1}$) indicates that the Ca^{2+} ion has only one oxidation state; titanium is capable of forming variable oxidation states due to the presence of valence electrons in the d-shell; it can form stable high and low oxidation states;
12. $[\text{Ni}(\text{H}_2\text{O})_6][\text{BF}_4]_2$ is colored as the Ni^{2+} ion has the electronic configuration of $1s^2 2s^2 2p^6 3s^2 3p^6 3d^8$; the color of transition metal ions is associated with partially filled d orbitals; the d-to-d electronic transition is the origin of the color of transition metal complexes; it is only possible to have these transitions if the transition metal has the partially filled d-orbital;

13. a) [Ar] 3d⁶

b) octahedral transition metal complex



- c) the ligand and the transition metal in this complex forms coordinate bonds: unlike typical covalent bonding, in coordinate bonding the pair of electrons comes from the same atom, in this case the bidentate ligand ethanedioate;
- d) ethanedioate ion is a bidentate ligand; ligands may have different charge densities; for example, the ethanedioate ligand, C₂O₄²⁻, has a lower charge density compared to water, H₂O, and the crystal field splitting caused by ethanedioate ion will be diminished; the configuration adopted involves a spin-paired arrangement (see figure 3 on page 322);
- e) the complex is paramagnetic as the Fe²⁺ cation has four unpaired electrons;

14. According to IUPAC, a transition element is an element that has an atom with an incomplete d-sublevel or that gives rise to cations with an incomplete d-sublevel.

Hg has an condensed electron configuration of [Xe] 4f¹⁴ 5d¹⁰ 6s²

At first glance, the formation of HgF₄ must involve electrons in the 5d (or maybe even 4f) subshell of mercury (see note below), which is typical for transition elements; however, only minute quantities of HgF₄ were detected under extreme conditions, and the detection technique (IR spectrometry) was ambiguous, so the very existence of HgF₄ is questionable; even if this compound really exists, it is only a single example, which is insufficient for classifying mercury as a transition element.

Note: the formation of four bonds between mercury and fluorine could also involve only the outer electron shells of both elements; such a phenomenon, known as hypervalence, is common for many non-transition elements; in this case, the existence of HgF₄ does not suggest that mercury is a transition element.

Jensen, however, argues that the synthesis of HgF₄ can only occur under non-standard (non-equilibrium) conditions, under which obtaining direct compositional and structural evidence for HgF₄ becomes extremely challenging; he also argues that the classification employed in the periodic table reflects those properties of elements most likely to be observed under standard laboratory conditions – conditions under which, as discussed above, mercury is known to retain all its electrons in the 5d orbitals (5d¹⁰); hence, it would be misleading to suggest that Hg is better described as a transition element, as this does not occur under standard conditions.



Topic 14 – Chemical bonding and structure (AHL)

End of topic questions (page 355)

1. C;

$$\text{FC(P)} = (5) - \frac{1}{2}(10) - 0 = 0$$

$$\text{FC(O)}_{\text{single bond}} = (6) - \frac{1}{2}(2) - 6 = -1$$

$$\text{FC(O)}_{\text{double bond}} = (6) - \frac{1}{2}(4) - 4 = 0$$

$$\Delta\text{FC} = 0 + (-1) + 0 = -1$$

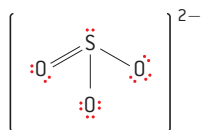
2. D;

$$\text{FC(C)} = (4) - \frac{1}{2}(8) - 0 = 0$$

$$\text{FC(O)} = (6) - \frac{1}{2}(4) - 4 = 0$$

$$\Delta\text{FC} = 0$$

3. C; the sulfite oxyanion is an AB_3E system that has four electron domains (tetrahedral geometry) and a molecular geometry of trigonal pyramidal;



$$\text{FC(S)} = 6 - \frac{1}{2}(8) - 2 = 0$$

$$\text{FC(O}_1) = 6 - \frac{1}{2}(4) - 4 = 0$$

$$\text{FC(O}_2) = 6 - \frac{1}{2}(2) - 6 = 0$$

4. D; the bromine atom has 7 valence electrons; when it is the central atom in an AB_5E system, it has sp^3d^2 hybridization; with 6 electron domains it has an octahedral electronic geometry and a square-based pyramidal molecular geometry;
5. D; the phosphorus atom has five valence electrons available for bonding; the additional electrons in phosphorus pentafluoride ion enable the phosphorus atom to form six covalent bonds with fluorine atoms; it is an AB_6 system and the phosphorus atom has sp^3d^2 hybridization; with no lone-pairs, its electronic and molecular geometry are both octahedral;
6. D; non-polar molecules are the result of the molecule having a net-dipole of zero; this can be achieved in a number of ways; in each case the molecular geometry must be examined, with particular attention paid to the presence of lone-pair of electrons and their position within the molecular structure

	System	Electronic geometry	Molecular geometry	Polarity
SF_4	AB_4E	Trigonal bipyramidal	See Saw	Polar
ClF_3	AB_3E_2	Trigonal bipyramidal	T Shaped	Polar
BrCl_5	AB_5E	Octahedral	Square-based pyramid	Polar
SeF_6	AB_6	Octahedral	Octahedral	Non-polar



7. B; for atomic orbitals to overlap and form molecular orbitals they must be relatively close in energy and the symmetry of the atomic orbitals must be identical; a number x atomic orbitals combine to form x new molecular orbitals; there are three possible outcomes:

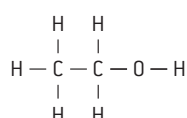
- bonding orbital: sigma (σ) or pi (π) orbital
- anti-bonding orbital: sigma star (σ^*) or pi star (π^*) orbital
- non-bonding situation.

I. this combination of p-orbitals will create a sigma (σ) bond;

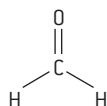
II. this combination of p-orbitals result in anti-bonding as the symmetry of the orbitals is not identical;

III. this combination of an s and p-orbital will result in a sigma (σ) bond as they are relatively close in energy and their symmetry enables direct head-on overlap of the atomic orbitals;

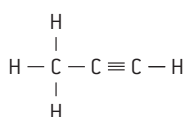
8. C; the oxygen atom has six valence electrons and in ethanol it forms two sigma (σ) bonds; there are additional two lone-pair electrons present on the oxygen atom; the electronic geometry of the oxygen atom is tetrahedral and the hybridization will be sp^3



9. B; methanal contains the carbonyl group $\text{C}=\text{O}$; the carbon atom is forming three sigma (σ) bonds and one pi bond (π); the carbonyl group is made up of a carbon-oxygen double bond, a sigma plus pi bond ($\sigma + \pi$); a π bond is formed from the sideways overlap of the two p_z unhybridized atomic orbitals, with the overlap regions above and below the internuclear axis B; the hybridization required for the carbon atom is sp^2 ;



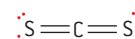
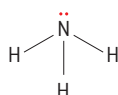
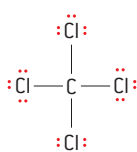
10. B; this molecule of propyne contains, in total, 6 sigma bonds and 2 pi bonds; a triple bond is composed of 1 sigma bonds and 2 pi bonds;



11. a)

	CCl_4	NH_3	CS_2
(i)	Tetrahedral	Tetrahedral	Linear
(ii)	Tetrahedral	Trigonal pyramidal	Linear
(iii)	109.5°	107°	180°
(iv)	sp^3	sp^3	sp
(v)	Non-polar	Polar	Non-polar

b)



$$\text{FC}(\text{C}) = (4) - \frac{1}{2}(8) - 0 = 0$$

$$\text{FC}(\text{N}) = (5) - \frac{1}{2}(6) - 2 = 0$$

$$\text{FC}(\text{C}) = (4) - \frac{1}{2}(8) - 0 = 0$$

$$\text{FC}(\text{Cl}) = (7) - \frac{1}{2}(2) - 6 = 0$$

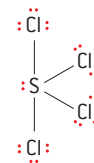
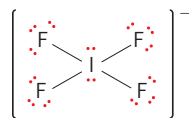
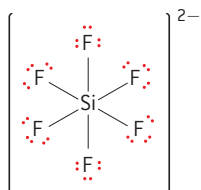
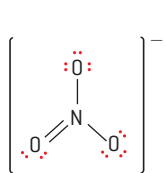
$$\text{FC}(\text{H}) = (1) - \frac{1}{2}(2) - 0 = 0$$

$$\text{FC}(\text{S}) = (6) - \frac{1}{2}(4) - 4 = 0$$



12.

	$[\text{NO}_3]^-$	$[\text{SiF}_6]^{2-}$	$[\text{IF}_4]^-$	SCl_4
(i)	Trigonal planar	Octahedral	Octahedral	Trigonal bipyramidal
(ii)	Trigonal planar	Octahedral	Square planar	See Saw
(iii)	109.5°	90°	90°	$>90^\circ/120^\circ$



$$\text{FC}(\text{N}) = (5) - \frac{1}{2}(8) - 0 = 1$$

$$\text{FC}(\text{Si}) = (4) - \frac{1}{2}(12) - 0 = -2$$

$$\text{FC}(\text{F}) = (7) - \frac{1}{2}(2) - 6 = 0$$

$$\text{FC}(\text{Cl}) = (7) - \frac{1}{2}(2) - 6 = 0$$

$$\text{FC}(\text{O}_1) = (6) - \frac{1}{2}(4) - 4 = 0$$

$$\text{FC}(\text{F}) = (7) - \frac{1}{2}(2) - 6 = 0$$

$$\text{FC}(\text{S}) = (6) - \frac{1}{2}(8) - 2 = 0$$

$$\text{FC}(\text{O}_2) = (6) - \frac{1}{2}(2) - 6 = -1$$

$$\text{FC}(\text{I}) = (7) - \frac{1}{2}(8) - 4 = -1$$

13. Reaction II requires a shorter wavelength; O_2 has double bond/bond order 2 and O_3 intermediate between double and single bonds/bond order of $1\frac{1}{2}$.



Topic 15 – Energetics and thermochemistry (AHL)

Quick questions

Page 363

$$\begin{aligned}\Delta H_{\text{sol}} &= \Delta H_{\text{lat}}(\text{BaCl}_2) + \Delta H_{\text{hyd}}(\text{Ba}^{2+}) + 2[\Delta H_{\text{hyd}}(\text{Cl}^-)] \\ &= 2069 + (-1346) + 2 \times (-359) \text{ kJ mol}^{-1} = 5 \text{ kJ mol}^{-1}\end{aligned}$$

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1. a) positive

b) negative

c) positive

d) positive

e) negative

2. reactants entropy: $214 + (4 \times 131) = 738$

products entropy: $186 + (2 \times 189) = 564$

$$\Delta S^\ominus = (564 - 738) = -174 \text{ J K}^{-1} \text{ mol}^{-1}$$

sign should be negative because of increase in order/decrease in disorder; fewer moles of gas on right;

Page 370

a) $-81.8 \text{ kJ mol}^{-1}$

b) -8.4 kJ mol^{-1}

c) -5.9 kJ mol^{-1}



End of topic questions (page 373)

1. a) **I:** atomization/sublimation (of Mg)/ $\Delta H_{\text{atomization}}^{\ominus}(\text{Mg})/\Delta H_{\text{sublimation}}^{\ominus}(\text{Mg})$;
V: enthalpy change of formation of $(\text{MgCl}_2)/\Delta H_{\text{formation}}^{\ominus}(\text{MgCl}_2)$;
b) Energy value for **II:** +243;
 Energy value for **III:** $738 + 1451 = 2189$;
 Energy value for **IV:** $2 \times (-349)$;
 $\Delta H_{\text{lat}}^{\ominus}(\text{MgCl}_2) = 642 + 148 + 243 + 2189 = (+)2252 \text{ KJ}$
c) theoretical value assumes ionic model; experimental value greater due to (additional) covalent character;
d) oxide greater charge; oxide smaller radius;
2. B
3. B
4. B
5. C
6. a reaction is spontaneous when $\Delta G^{\ominus}$ is negative and non-spontaneous when $\Delta G^{\ominus}$ is positive;
 at high T, $\Delta G^{\ominus}$ is negative (because) $T\Delta S^{\ominus}$ is greater than $\Delta H^{\ominus}$; at low T, $\Delta G^{\ominus}$ is positive because $T\Delta S^{\ominus}$ is smaller than $\Delta H^{\ominus}$;
7. a) the enthalpy/energy/heat change for the formation of one mole of a compound/substance from its elements in their standard states/under standard conditions/at 298 K and 1 atm;

$$\frac{1}{2}\text{H}_2(\text{g}) + \frac{1}{2}\text{N}_2(\text{g}) + 1\frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{HNO}_3(\text{l})$$

b) $\Delta H_{\text{r}} = \sum \Delta H_{\text{f}}^{\ominus}(\text{products}) - \sum \Delta H_{\text{f}}^{\ominus}(\text{reactants})/\text{suitable cycle}$

$$= 3 \times (-394) + 2 \times (-286) - 185 = -1939 \text{ kJ}$$

c) negative; decrease in disorder/increase in order; 5 mol of gas $\rightarrow$ 3 mol of gas/reduction in number of gas moles.



Topic 16 – Chemical kinetics (AHL)

End of topic questions (page 387)

1. C; in order to solve this question we can use the working method to deduce the rate equation from the method of initial rates:

$$\frac{\text{rate 1}}{\text{rate 2}} = \frac{(0.10)^x (0.10)^y}{(0.20)^x (0.10)^y} = \frac{1.0 \times 10^{-6}}{4.0 \times 10^{-6}} = (0.5)^x = 0.25, \text{ so } x = 2;$$

$$\frac{\text{rate 2}}{\text{rate 3}} = \frac{(0.20)^x (0.10)^y}{(0.20)^x (0.40)^y} = \frac{4.0 \times 10^{-6}}{4.0 \times 10^{-6}} = (0.25)^y = 1, \text{ so } y = 0;$$

the reaction is second order with respect to Br_2 :

$$\text{rate} = k[\text{Br}_2]^2$$

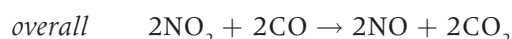
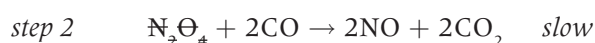
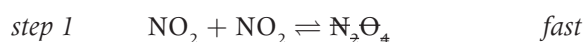
2. C;

$$\frac{\text{rate 1}}{\text{rate 2}} = \frac{(0.002)^x (0.01)^y}{(0.004)^x (0.01)^y} = \frac{4.0 \times 10^{-4}}{8.0 \times 10^{-4}} = (0.5)^x = 0.50, \text{ so } x = 1;$$

$$\frac{\text{rate 2}}{\text{rate 3}} = \frac{(0.004)^x (0.01)^y}{(0.004)^x (0.02)^y} = \frac{8.0 \times 10^{-4}}{1.6 \times 10^{-3}} = (0.50)^y = 0.5, \text{ so } y = 1;$$

the reaction is first order with respect to NO_2 and F_2 ;

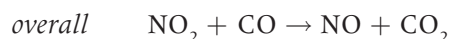
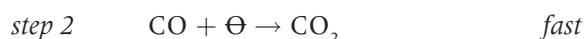
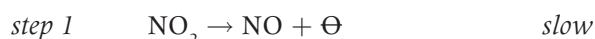
3. C; reactions may occur by more than one step and the slow step determines the rate of the reaction; the slow step is termed the rate-determining step (RDS); this is the step with the highest activation energy;
4. B; in a rate-concentration plot for a second order reaction (figure (b)), the rate is directly proportional to the square of the concentration, because $\text{rate} = k[\text{A}]^2$ for a second order reaction;
5. D;



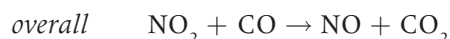
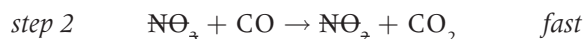
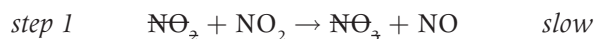
this mechanism does not result in the reaction in question;



this mechanism with one RDS, the rate expression is $\text{rate} = k[\text{NO}_2][\text{CO}]$;

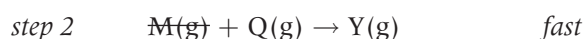
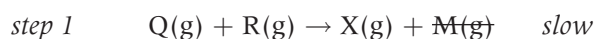


this mechanism does produce the correct overall equation but not the correct rate expression;



this mechanism does produce the correct overall equation and the correct rate expression;

6. D;

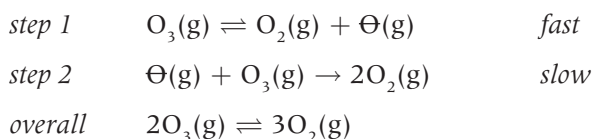


$$\text{rate} = k[\text{Q}][\text{R}];$$

an analysis of the working above determines that all three statements are valid;



7. D; the iodine atom is a reaction intermediate; be careful that this does not mask the fact that iodine (I) is important in the understanding of this mechanism; as a reaction intermediate, it is formed in the initial *fast* step and is consumed in the subsequent *slow* step; however, its formation and presence in the slow step is dependent on its formation from the iodine molecule (I_2) in the first fast step and for this reason the iodine molecule must be included in the rate expression; the other species in the rate expression will be the hydrogen molecule, hence the rate expression is $\text{rate} = k[I_2][H_2]$;
8. D; the frequency factor is essentially the number of times reactants will approach the activation energy barrier in unit time; the units of the frequency factor (A) are identical to those of the rate constant (k) and will vary depending on the order of the reaction; if the reaction is a first order reaction, the units will be s^{-1} ; this is why answer C may be chosen by mistake;
9. A;



In this mechanism, the reaction intermediate is the oxygen atom (O) as it is produced and then consumed in a subsequent step; as its presence in the slow step is dependent on the fast step, the reactant of the fast step must be included in the rate expression; therefore, the rate expression for this mechanism is $\text{rate} = k[O_3]^2$ and not as stated in statement III;

$$10. \text{ a) } \frac{\text{rate 1}}{\text{rate 2}} = \frac{(0.0150)^a (0.0150)^b}{(0.0150)^a (0.0300)^b} = \frac{2.32 \times 10^{-3}}{4.64 \times 10^{-3}} = (0.500)^b = 0.50, \text{ so } b = 1$$

$$\frac{\text{rate 1}}{\text{rate 3}} = \frac{(0.0150)^a (0.0150)^b}{(0.0300)^a (0.0150)^b} = \frac{2.32 \times 10^{-3}}{4.64 \times 10^{-3}} = (0.500)^a = 0.5, \text{ so } a = 1$$

the reaction is first order with respect to A and B; the overall reaction order is second order;

$$\text{b) } \text{rate} = k[A][B]$$

$$\text{c) } k = \frac{\text{rate}}{[A][B]}$$

$$K = \frac{4.64 \times 10^{-3} \text{ mol dm}^{-3} \text{ s}^{-1}}{1.50 \times 10^{-2} \text{ mol dm}^{-3} \times 3.00 \times 10^{-2} \text{ mol dm}^{-3}} = 1.03 \times 10^1 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$$

$$\text{d) } \text{rate} = k[A][B]$$

$$\begin{aligned} &= (1.03 \times 10^1 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}) \times (2.00 \times 10^{-2} \text{ mol dm}^{-3}) \times (4.00 \times 10^{-2} \text{ mol dm}^{-3}) \\ &= 8.25 \times 10^{-3} \text{ mol dm}^{-3} \text{ s}^{-1} \end{aligned}$$

$$11. \text{ a) } E_a = \frac{\ln \frac{6.30 \times 10^3}{2.25 \times 10^3} \times 8.31}{\frac{1}{356} - \frac{1}{305}} = \frac{-29.7}{-4.70 \times 10^{-4}} = 6.33 \times 10^4 \text{ J mol}^{-1}$$

$$\text{b) } 6.33 \times 10^4 = \frac{\ln \frac{k_3}{6.30 \times 10^3} \times 8.31}{\frac{1}{305} - \frac{1}{293}}$$

In the above expression, use the value of k_2 and the temperature for k_1 ; the combination should be either k_1 and T_1 , or k_2 and T_2 ;

$$\ln \frac{k_3}{6.30 \times 10^3} = -1.02286$$

$$\ln k_3 = -1.02286 + \ln(6.30 \times 10^3) = 7.72544$$

$$k_3 = 2.27 \times 10^3 \text{ s}^{-1}$$



There is an alternative method; retain a large number of significant figures in the intermediate values:

$$\ln k_1 = \ln A - \frac{E_a}{RT_1}$$

$$\ln A = \ln k_1 + \frac{E_a}{RT_1} = \ln(6.30 \times 10^3) + \frac{63300}{8.31 \times 305} = 33.7231$$

$$\ln k_3 = \ln A - \frac{E_a}{RT_3} = 33.7231 - \frac{63300}{8.31 \times 293} = 7.7254$$

$$k_3 = 2.27 \times 10^3 \text{ s}^{-1}$$



Topic 17 – Equilibrium (AHL)

End of topic questions (page 394)

1. a) $K_c = \frac{[\text{SO}_2\text{Cl}_2]}{[\text{Cl}_2][\text{SO}_2]}$
 b) 12.5;
 c) value of K_c increases; $[\text{SO}_2\text{Cl}_2]$ increases; decrease in temperature favours (forward) reaction which is exothermic;
 d) no effect on the value of K_c as it depends only on temperature; $[\text{SO}_2\text{Cl}_2]$ decreases; increase in volume favours the reverse reaction which has more gaseous moles;
 e) no effect; catalyst increases the rate of forward and reverse reactions (equally)/catalyst decreases activation energies (equally);
2. $2\text{NO}(\text{g}) + 2\text{H}_2(\text{g}) \leftrightarrow \text{N}_2(\text{g}) + 2\text{H}_2\text{O}(\text{g})$

	NO (g)	H ₂ (g)	N ₂ (g)	H ₂ O (g)
Initial (mol dm ⁻³)	0.100	0.051	0.000	0.100
Change (mol dm ⁻³)	-0.038	-0.038	+0.019	+0.038
Equilibrium (mol dm ⁻³)	0.062	0.013	0.019	0.138

$[\text{H}_2]$ at equilibrium = 0.013 mol dm⁻³

$[\text{N}_2]$ at equilibrium = 0.019 mol dm⁻³

$[\text{H}_2\text{O}]$ at equilibrium = 0.138 mol dm⁻³

$$K_c = \frac{[\text{N}_2][\text{H}_2\text{O}]^2}{[\text{NO}]^2 [\text{H}_2]^2} = \frac{(0.019)(0.138)^2}{(0.062)^2(0.013)^2} = 5.6 \times 10^2$$



Topic 18 – Acids and bases (AHL)

End of topic questions (page 410)

1. A
2. C
3. A
4. a) acidic and $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ is a weak acid;

$$[\text{Fe}(\text{H}_2\text{O})_6]^{3+} (\text{aq}) \rightarrow [\text{Fe}(\text{OH})(\text{H}_2\text{O})_5]^{2+} (\text{aq}) + \text{H}^+ (\text{aq})$$
 b) neutral and NaNO_3 (sodium nitrate) is formed from strong base and strong acid; ions do not hydrolyze;
 c) alkaline and CO_3^{2-} is a weak base;

$$\text{CO}_3^{2-} (\text{aq}) + \text{H}_2\text{O} (\text{l}) \rightarrow \text{HCO}_3^- (\text{aq}) + \text{OH}^- (\text{aq})$$
5. C
6. a) NH_3 weak(er) base; partial dissociation;
 $[\text{OH}^-] < 0.1(0)/\text{pOH} > 1$ (thus $\text{pH} < 13$ / $\text{pH} + \text{pOH} = 14$);
 b) around $\text{pH} = 5$;
 strong acid–weak base titration, thus acidic; at equivalence point, NH_4^+ present is acidic;

$$\text{NH}_4^+ \leftrightarrow \text{NH}_3 + \text{H}^+$$
 c) $\text{NH}_3 (\text{aq}) + \text{H}_2\text{O} (\text{l}) \leftrightarrow \text{NH}_4^+ (\text{aq}) + \text{OH}^- (\text{aq})$

$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]}$$
 d) $[\text{NH}_3] = [\text{NH}_4^+]$
 e) $\text{pOH} = 14.00 - 9.25 = 4.75$

$$\text{p}K_b (= \text{pOH}) = 4.75$$

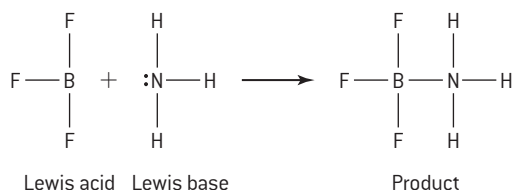
$$K_b = 1.78 \times 10^{-5}$$
 f) optimum/most effective/highest buffer capacity/50%–50% buffer/equally effective as an acidic buffer and a basic buffer;
7. A
8. D
9. D
10. Brønsted-Lowry acid: proton donor; CH_3COOH and H_3O^+
 Lewis base: electron pair donor; H_2O and CH_3COO^- ;
11. a) donates a proton (H^+ ion)
 b) (acid) (conjugate base)

$$\begin{array}{cc} \text{H}_2\text{O} & \text{OH}^- \\ \text{NH}_4^+ & \text{NH}_3 \end{array}$$
 c) Lewis acid accepts an electron pair, while a Lewis base donates an electron pair;
 F^- is the base; BF_3 is the acid;



12. a) a Lewis acid: electron pair acceptor; example: AlCl_3 , BF_3 etc.;

b) structural formula of Lewis acid (e.g. BF_3 , AlCl_3 , transition element etc.); structural formula of Lewis base (e.g. NH_3 , H_2O etc.); structural formula of product (e.g. F_3BNH_3 etc.); dative covalent (bond)/coordinate (bond);



13. A

14. C

15. C

16. D

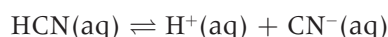
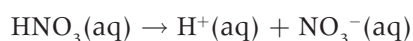
$$17. K_b = \frac{[\text{OH}^-]^2}{[\text{NH}_3]} = 10^{-4.75} = 1.78 \times 10^{-5}$$

$$[\text{OH}]^- = \sqrt{1.00 \times 10^{-2} \times 10^{-4.75}} = 4.22 \times 10^{-4} \text{ mol dm}^{-3}; \text{pOH} = -\log_{10} (4.22 \times 10^{-4}) = 3.37$$

$$[\text{H}]^+ = \frac{1.00 \times 10^{-14}}{4.22 \times 10^{-4}} = 2.37 \times 10^{-11}$$

$$\text{pH} = 14 - 3.37 = 10.6;$$

18. a) strong acid completely dissociated(ionized) and weak acid partially dissociated (ionized);



$$\text{b) } K_a = \frac{[\text{H}^+][\text{CN}^-]}{[\text{HCN}]}$$

$$K_a = 10^{-9.21} = 6.17 \times 10^{-10}$$

$$\text{c) } [\text{H}^+] = \sqrt{k_a[\text{HCN}]} / \sqrt{(6.17 \times 10^{-10} \times 0.108)} = 8.16 \times 10^{-6}$$

$$\text{pH} = 5.09;$$

or

$$\text{pH} = \frac{1}{2} (\text{p}K_a - \log[\text{HCN}]) / \frac{1}{2} (9.21 - \log 0.108) = 5.09$$

$$[\text{H}^+] = 10^{-5.09} = 8.16 \times 10^{-6} \text{ assume } [\text{H}^+] \ll 0.108; \text{negligible dissociation;}$$

$$19. \text{a) } [\text{H}^+] = \frac{1.00 \times 10^{-14}}{1.28 \times 10^{-3}} = 7.81 \times 10^{-12} \text{ mol dm}^{-3}$$

$$\text{pOH} = -\log 1.28 \times 10^{-3} = 2.90$$

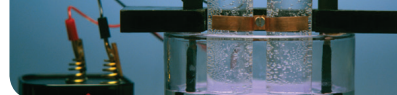
$$\text{pH} = (14.0 - 2.90) = 11.1$$

$$\text{b) } K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = \frac{(1.28 \times 10^{-3})^2}{0.100 - 0.00128} / \frac{(1.28 \times 10^{-3})^2}{0.100} = 1.66 \times 10^{-5}$$

20. A

21. A

22. C



Topic 19 – Redox processes (AHL)

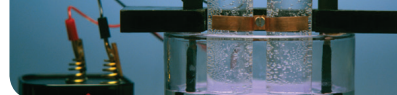
Quick questions

Page 427

The sludge might contain other metals, such as silver, gold and platinum; these elements can be extracted from the sludge by chemical reagents, reduced and isolated as individual metals; therefore, the price of the sludge is often higher than that of copper;

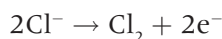
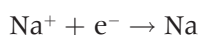
Page 429

Pure water is a very weak conductor of electricity, so an electrolyte is needed for the electrolysis of water; dilute H_2SO_4 is a strong acid, so it fully dissociates in aqueous solutions and produces enough ions (carriers of electrical charge) for the electrolysis to proceed; in addition, the anion of sulfuric acid, $\text{SO}_4^{2-}(\text{aq})$, does not undergo any chemical changes during the electrolysis, so it does not need to be replaced;



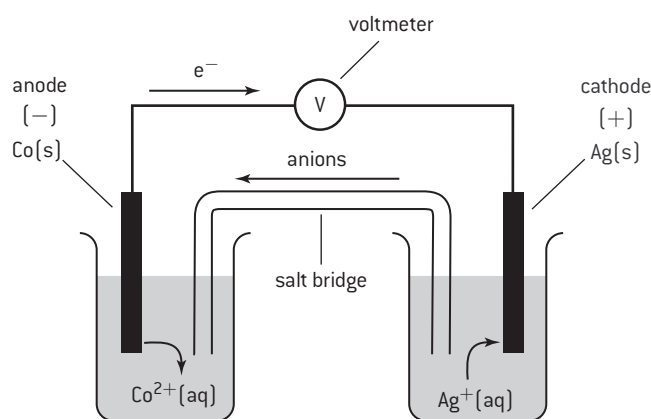
End of topic questions (page 434)

1. D; these three conditions constitute the definition of a standard cell;
2. A; zinc is less active than magnesium, so zinc can neither substitute magnesium (answer C is incorrect) or from a salt (answer D is incorrect) under these conditions; to displace chlorine, a more active halogen (not metal) is needed, so answer B is also incorrect; please note, however, that the solution of magnesium chloride is slightly acidic (due to hydrolysis), so zinc might slowly react with water to produce hydrogen gas;
3. D; aluminium is more active than nickel, so Al(s) will be oxidized to $\text{Al}^{3+}(\text{aq})$ while $\text{Ni}^{2+}(\text{aq})$ will be reduced to Ni(s) ; the standard cell potential will be equal to the difference of the standard half-cell potentials: $E^\ominus = -0.23 - (-1.66) = 1.43 \text{ V}$
4. B; in both cases, elemental bromine will be produced at the anode; in the case of molten magnesium bromide, only magnesium metal can be produced at the cathode; in contrast, the electrolysis of aqueous magnesium bromide will produce hydrogen gas at the cathode;
5. C; the reduction of $\text{Ag}^+(\text{aq})$ to Ag(s) can take place only at the negative electrode (cathode);
6. B; to answer this question, we need to look at the half-equations (the states are omitted):

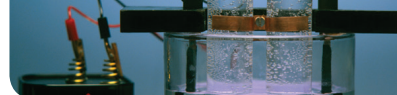


since the same quantity of electricity was used, the amounts of products will be inversely proportional to the numbers of electrons involved in the half-equations: $n(\text{Na}) = 2n(\text{Br}_2) = 2n(\text{Mg}) = 2n(\text{Cl}_2)$

7. A; according to Faraday's Law, $Q = \frac{z \times F \times m}{M}$, where $Q = I \times t$; therefore, $I \times t = \frac{z \times F \times m}{M}$ and so $m = \frac{M \times I \times t}{z \times F}$; for $\text{Cu}^{2+}(\text{aq})/\text{Cu(s)}$, $M = 63.55 \text{ g mol}^{-1}$ and $z = 2$; finally, $t = 60 \times 60 = 3600 \text{ s}$, $I = 1 \text{ A}$, and $F = 96\,500 \text{ C mol}^{-1}$
8. the voltaic cell can be represented as follows:



- (i) *cathode (positive electrode):* $\text{Ag}^+(\text{aq}) + \text{e}^- \rightarrow \text{Ag(s)}$
anode (negative electrode): $\text{Co(s)} \rightarrow \text{Co}^{2+}(\text{aq}) + 2\text{e}^-$
- (ii) $\text{Co(s)} + 2\text{Ag}^+(\text{aq}) \rightarrow \text{Co}^{2+}(\text{aq}) + 2\text{Ag(s)}$
- (iii) $\text{Co(s)} \mid \text{Co}^{2+}(\text{aq}) \parallel \text{Ag}^+(\text{aq}) \mid \text{Ag(s)}$
- (iv) electrons move from the cobalt electrode (anode) to the silver electrode (cathode) through the external circuit; the $\text{Co}^{2+}(\text{aq})$ ions are formed from Co(s) at the anode and move into the aqueous solution in the left hand side beaker; the $\text{Ag}^+(\text{aq})$ ions in the aqueous solution

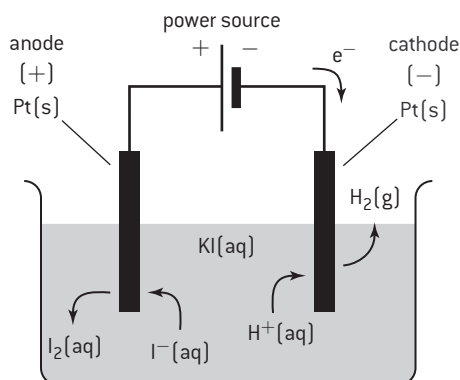


in the right hand side beaker move towards the silver cathode and form Ag(s) ; the counter-ions (anions) move through the salt bridge from the right hand side beaker to the left hand side beaker;

(v) according to the *IB Data Booklet*, the $E^\ominus$ for $\text{Ag}^+(\text{aq})/\text{Ag(s)}$ is $+0.80\text{ V}$; therefore, the cell potential is $+0.80 - (-0.28) = 1.08\text{ V}$

(vi) $\Delta G^\ominus = -nFE^\ominus = -2 \times 96\,500 \times 1.08 \approx -208\,000\text{ J} = -208\text{ kJ}$

9. The electrolytic cell can be represented as follows:



Note 1: depending on the experimental conditions, elemental iodine can be produced as $\text{I}_2(\text{aq})$ or $\text{I}_2(\text{s})$, or both;

Note 2: elemental iodine is readily soluble in concentrated KI(aq) due to the formation of triiodide anions: $\text{I}^-(\text{aq}) + \text{I}_2(\text{aq}) \rightleftharpoons \text{I}_3^-(\text{aq})$; this reaction is discussed in Options B.4 and C.8; it is not required for AHL;

(i) *cathode (negative electrode):* $2\text{H}_2\text{O(l)} + 2\text{e}^- \rightarrow \text{H}_2(\text{g}) + 2\text{OH}^-(\text{aq})$

anode (positive electrode): $2\text{I}^-(\text{aq}) \rightarrow \text{I}_2(\text{aq}) + 2\text{e}^-$

or

$3\text{I}^-(\text{aq}) \rightarrow \text{I}_3^-(\text{aq}) + 2\text{e}^-$

overall cell reaction: $2\text{H}_2\text{O(l)} + 2\text{I}^-(\text{aq}) \rightarrow \text{H}_2(\text{g}) + \text{I}_2(\text{aq}) + 2\text{OH}^-(\text{aq})$

or

$2\text{H}_2\text{O(l)} + 3\text{I}^-(\text{aq}) \rightarrow \text{H}_2(\text{g}) + \text{I}_3^-(\text{aq}) + 2\text{OH}^-(\text{aq})$

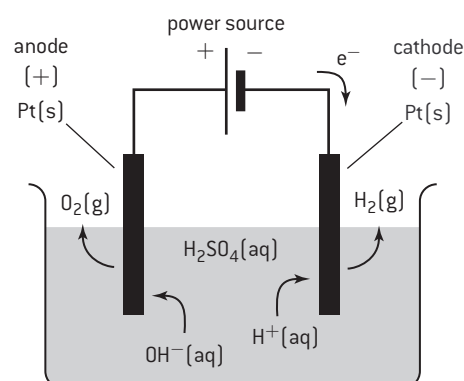
Note: the equations involving triiodide ions are not required for AHL;

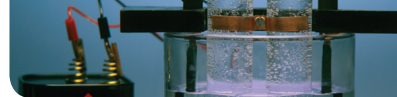
(ii) any inert conducting material, such as platinum or graphite;

(iii) electrons move from the anode to the cathode through the external circuit; the $\text{I}^-(\text{aq})$ ions move to the anode; the $\text{H}^+(\text{aq})$ ions (produced from water) move to the cathode;

(iv) at the anode, the initially colourless solution will turn first yellow, then orange, and finally brown due to the formation of $\text{I}_2(\text{aq})$ and $\text{I}_3^-(\text{aq})$ ions; at high electric currents, the formation of grey-coloured precipitate of $\text{I}_2(\text{s})$ can be observed; at the cathode, bubbles of hydrogen gas will be formed;

10. a)





b) *cathode (negative electrode):* $2\text{H}^+(\text{aq}) + 2\text{e}^- \rightarrow \text{H}_2(\text{g})$

anode (positive electrode): $2\text{H}_2\text{O}(\text{l}) \rightarrow \text{O}_2(\text{g}) + 4\text{H}^+(\text{aq}) + 4\text{e}^-$

overall cell reaction: $2\text{H}_2\text{O}(\text{l}) \rightarrow 2\text{H}_2(\text{g}) + \text{O}_2(\text{g})$

c) electrons move from the anode to the cathode through the external circuit; the $\text{H}^+(\text{aq})$ ions move to the cathode; the $\text{OH}^-(\text{aq})$ ions (produced from water) move to the anode;

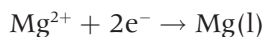
d) according to Faraday's Law, $Q = z \times F \times n$, where $Q = I \times t$ and $n = \frac{V}{V_M}$; therefore,
 $I \times t = \frac{z \times F \times V}{V_M}$; and so $V = \frac{I \times t \times V_M}{z \times F}$; according to the *IB Data Booklet*, the molar volume of ideal gas at STP (273 K and 100 kPa) is $22.7 \text{ dm}^3 \text{ mol}^{-1}$, so at SATP (298 K and 100 kPa),
 $V_M = \frac{22.7 \times 298}{273} \approx 24.8 \text{ dm}^3 \text{ mol}^{-1}$; finally, $F = 96\,500 \text{ C mol}^{-1}$ and $1 \text{ Q} = 1 \text{ A} \times 1 \text{ s}$, so the electrolysis duration must be converted to seconds: $5.00 \text{ h} \times 3600 \text{ s h}^{-1} = 1.80 \times 10^4 \text{ s}$; for $\text{H}_2(\text{g})$, $z = 2$ and so $V(\text{H}_2) = \frac{2.35 \times 1.80 \times 10^4 \times 24.8}{2 \times 96\,500} \approx 5.44 \text{ dm}^3$; according to the overall cell reaction in (b), the volume of oxygen will be twice as low (2.72 dm^3);

11. *tin cathode (negative electrode):* $\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Cu}(\text{s})$

copper anode (positive electrode): $\text{Cu}(\text{s}) \rightarrow \text{Cu}^{2+}(\text{aq}) + 2\text{e}^-$

Observations: the tin cathode changes colour from silvery to red, becomes thicker, and its mass gradually increases (due to copper deposition); the copper anode becomes thinner and its mass gradually decreases (due to copper passing into the solution); the blue colour of the solution does not change (as the amount of copper ions consumed at the cathode is equal to the amount of copper ions produced at the anode); the temperature of the solution may rise (as some electrical energy will be converted to heat due to non-zero electrical resistance of the electrolyte);

12. In the first cell, magnesium metal will be produced at the cathode (negative electrode):



Note: the state of the Mg^{2+} ion in molten MgCl_2 is difficult to define, so it is usually omitted.

In the second cell, the following processes will take place:

cathode (negative electrode): $2\text{H}_2\text{O}(\text{l}) + 2\text{e}^- \rightarrow \text{H}_2(\text{g}) + 2\text{OH}^-(\text{aq})$

anode (positive electrode): $4\text{OH}^-(\text{aq}) \rightarrow \text{O}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l}) + 4\text{e}^-$

overall cell reaction: $2\text{H}_2\text{O}(\text{l}) \rightarrow 2\text{H}_2(\text{g}) + \text{O}_2(\text{g})$

According to Faraday's Law, $\frac{2 \times m(\text{Mg})}{A_r(\text{Mg})} = \frac{2 \times m(\text{H}_2)}{M_r(\text{H}_2)} = \frac{4 \times m(\text{O}_2)}{M_r(\text{O}_2)}$, where the coefficients "2" and "4" are the numbers of electrons involved in respective half-equations; therefore,

$$m(\text{H}_2) = \frac{12.16 \times 2.02 \times 2}{24.31 \times 2} \approx 1.01 \text{ g and } m(\text{O}_2) = \frac{12.16 \times 32.00 \times 2}{24.31 \times 4} \approx 8.00 \text{ g.}$$



Topic 20 – Organic chemistry (AHL)

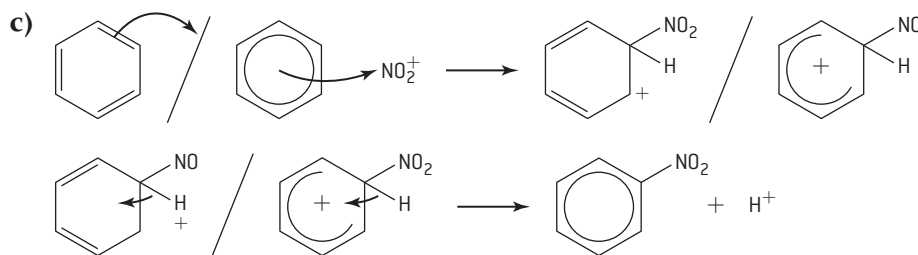
End of topic questions (page 459)

1. A

2. a) concentrated HNO_3 ; concentrated H_2SO_4 ;



or



3. B

4. B

5. D

6. D

7. A

8. a) $\text{C}_4\text{H}_9\text{Cl} + \text{KOH} \rightarrow \text{C}_4\text{H}_9\text{OH} + \text{KCl}$;

b) (substitution); nucleophilic; unimolecular

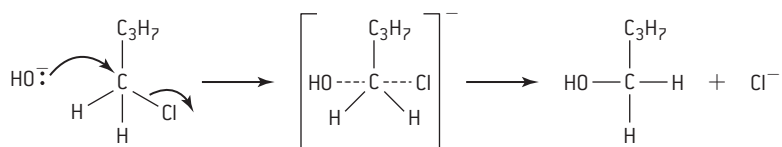
c) 1-chlorobutane:

$\text{S}_{\text{N}}2$;

2-chloro-2-methylpropane;

$\text{S}_{\text{N}}1$;

d) $\text{S}_{\text{N}}2$ 1-chlorobutane;

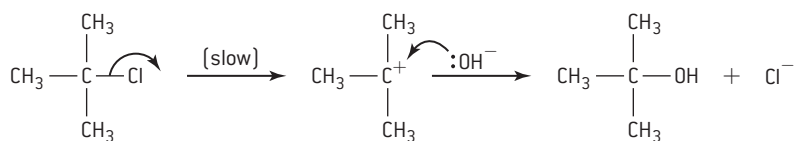


curly arrow going from lone pair or negative charge on O in OH^- to C;

curly arrow for C1 leaving;

formation of the transition state in bracket, with negative charge and dotted lines to represent bonds;

$\text{S}_{\text{N}}1$ 2-chloro-2-methylpropane-allow EFC from (iii)



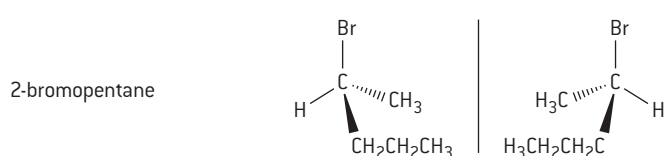
curly arrow showing C1 leaving;

formation of carbocation;

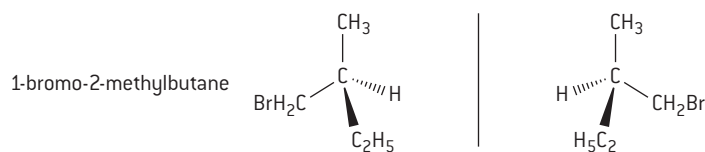
curly arrow from lone pair or negative charge on O in OH^- to C^+ ;



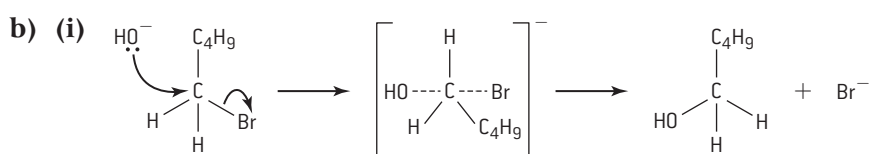
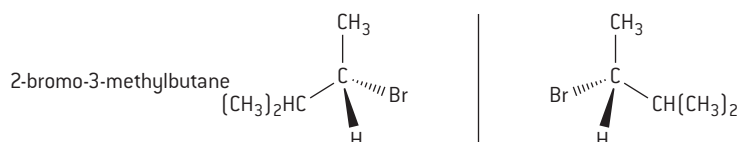
9. a)



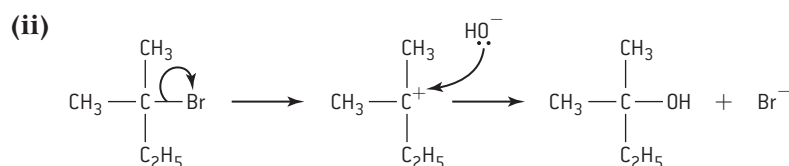
OR



OR



curly arrow going from lone pair/negative charge on O in HO^- to C bonded to Br; curly arrow from C–Br bond to form Br^- (this can also be shown in transition state; transition state showing overall negative charge);



curly arrow from C–Br bond to form Br^- ; correct structure of tertiary carbocation; curly arrow going from lone pair/negative charge on O in HO^- to C^+ ;

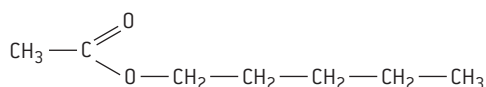
(iii) the C bonded to the Br in 1-bromopentane is also bonded to two H atoms so can accommodate five groups around it in the transition state;

the C bonded to the Br in 2-bromo-2-methylbutane has three other (bulky) groups bonded to it so cannot accommodate five groups around it in the transition; 2-bromo-2-methylbutane forms a tertiary carbocation which is stabilized by the positive inductive effect of the three alkyl groups;

1-bromopentane would form a primary carbocation (if it went by $\text{S}_{\text{N}}2$) which is much less stable as there is only one alkyl group exerting a positive inductive effect;

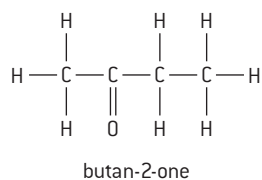
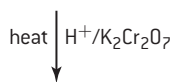
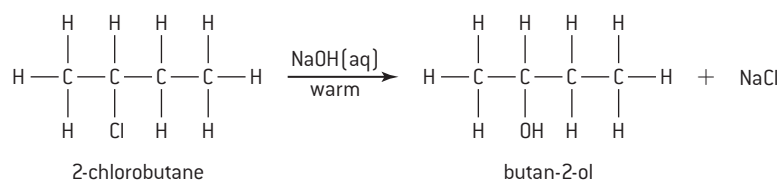
(iv) the boiling point of 1-bromopentane is higher than the boiling point of 2-bromo-2-methylbutane; 2-bromo-2-methylbutane is more spherical in shape; there is less surface area in contact between molecules of 2-bromo-2-methylbutane than between molecules of 1-; hence weaker intermolecular forces of attraction/van der Waals' forces of attraction between molecules of 2-bromo-2-methylbutane;

(v) esterification / condensation;

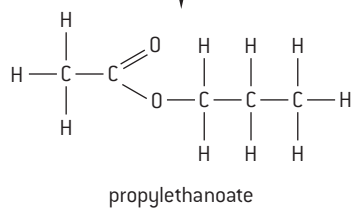
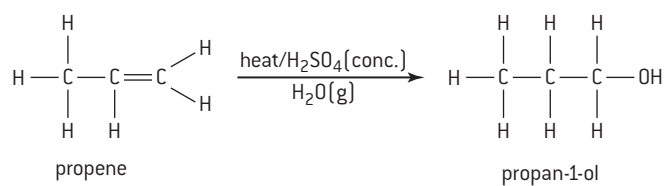




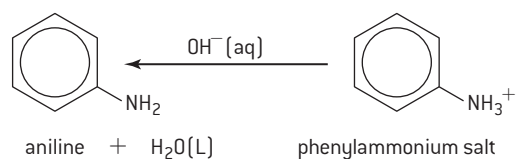
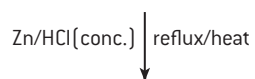
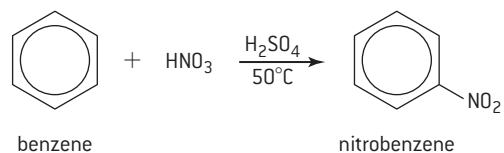
10. (i)

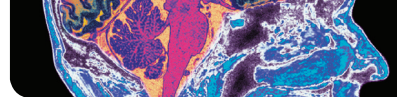


(ii)



(iii)





Topic 21 – Measurement and analysis (AHL)

Quick question (page 469)

The peaks with $\frac{m}{z} = 59$ and 60 are probably produced by the molecules of propanal that contain heavier isotopes of carbon (^{13}C instead of ^{12}C) and/or hydrogen (^2H instead of ^1H); other peaks (with $\frac{m}{z} = 69\text{--}75$) probably belong to some impurities in the analysed sample of propanal;

End of topic questions (page 470)

- The *IHD* (see Chapter 11) for $\text{C}_3\text{H}_6\text{O}_2$ is $3 - 0.5 \times 6 + 1 = 1$, so compound **X** contains either one double bond or one ring; the strong absorption at 1710 cm^{-1} in the IR spectrum suggests the presence of a carbonyl group, so the compound is probably acyclic; the signal at 11.7 ppm in the ^1H NMR spectrum and the peak with $\frac{m}{z} = 45$ in the mass spectrum suggest the presence of a COOH group, so compound **X** is a carboxylic acid; this is consistent with the IR spectrum, which shows a very broad absorption of the O–H bond in the 3000 cm^{-1} region.

Therefore, the formula of **X** is $\text{CH}_3\text{--CH}_2\text{--COOH}$ (propanoic acid).

Note: another possible structure, $\text{CH}_3\text{--CH}_2\text{--O--CHO}$ (ethyl formate), is inconsistent with the ^1H NMR spectrum (as the signal of the CHO group would appear at 9.4–10 ppm) and the IR spectrum (there would be no broad O–H absorption in the 3000 cm^{-1} region).

The spectroscopic information for compound **X** is summarized below:

IR spectrum

Absorption / cm^{-1}	Bond(s) involved
2800–3300 (strong, very broad)	O–H (in the hydrogen-bonded COOH group)
2900–3000 (several medium peaks)	C–H (in CH_2 and CH_3 groups)
1710 (strong)	C=O (in the COOH group)
1250 (strong)	probably C–O (in the COOH group)

^1H NMR spectrum

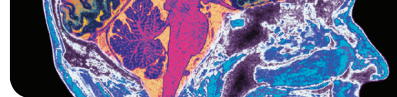
Chemical shift / ppm	Splitting pattern	Number of protons at adjacent atoms	Hydrogen environment
11.7	singlet	0	COOH
2.4	quartet	3	CH_2
1.1	triplet	2	CH_3

Mass spectrum

Peak with m/z of	Produced by	Due to the loss of
74	$\text{C}_3\text{H}_6\text{O}_2^{+\bullet}$ (molecular ion)	—
45	COOH^+	$\text{C}_2\text{H}_5^{\bullet}$
29	C_2H_5^+	$\text{COOH}^{\bullet}$

- The solutions for this and previous questions are similar: the *IHD* for $\text{C}_5\text{H}_{10}\text{O}_2$ ($5 - 0.5 \times 10 + 1 = 1$) and the strong absorption at 1700 cm^{-1} in the IR spectrum of **Y** suggest the presence of a carbonyl group; the signal at 11.4 ppm in the ^1H NMR spectrum and the broad absorption in the 3000 cm^{-1} region of the IR spectrum belong to a COOH group, so compound **Y** is also a carboxylic acid.

There are only two signals in the ^1H NMR spectrum of **Y**: if the H atom of the COOH group in $\text{C}_5\text{H}_{10}\text{O}_2$ produces the signal at 11.4 ppm, then the other nine H atoms must be in the same chemical environment (as they produce only one sharp signal at 1.2 ppm); in addition, the signal at 1.2 ppm is a singlet, so the molecule of **Y** must not contain any adjacent CH_x groups; such



an arrangement of atoms takes place in a *tert*-butyl group, $(\text{CH}_3)_3\text{C}-$; the presence of this group is consistent with the mass spectrum of **Y**, where the peak with $\frac{m}{z} = 57$ can be produced by a C_4H_9^+ ion.

Therefore, the formula of **Y** is $(\text{CH}_3)_3\text{C}-\text{COOH}$ (2,2-dimethylpropanoic acid).

The spectroscopic information for compound **Y** is summarized below:

IR spectrum

Absorption / cm^{-1}	Bond(s) involved
2800–3300 (strong, very broad)	O–H (in the hydrogen-bonded COOH group)
2900–3000 (several medium peaks)	C–H (in CH_3 groups)
1700 (strong)	C=O (in the COOH group)
1200 (strong)	probably C–O (in the COOH group)

^1H NMR spectrum

Chemical shift / ppm	Splitting pattern	Number of protons at adjacent atoms	Hydrogen environment
11.4	singlet	0	COOH
1.2	singlet	0	$(\text{CH}_3)_3\text{C}$

Mass spectrum

Peak with m/z of	Produced by	Due to the loss of
102	$\text{C}_5\text{H}_{10}\text{O}_2^{+\bullet}$ (molecular ion)	—
57	C_4H_9^+	$\text{COOH}^\bullet$



Option A – Materials

A.1 Quick questions (Page 473)

1. high melting point; not permeable to moisture; highly structured crystalline structure; ceramic;
2. these classifications are useful when this is the material to be used and the difference in type is important, such as wool vs cotton for water repellent capability, cooler in warm weather, etc.; in each case, the classification depends on the final use.

Page 474

1. a) (i) magnesium oxide average electronegativity: 2.35; manganese oxide average electronegativity: 2.5;
(ii) % covalent character for magnesium oxide: $30\% \pm 5\%$; % covalent character for manganese oxide: $40\% \pm 5\%$;
b) MgO ; higher ionic character, tighter packing, less likely to move under stress; high melting point of ionic substances compared to covalent substances; or close packing and tight ionic lattice, high MP due to this;
2. metal, glass, etc. are more familiar than composites, ceramics for recycling purposes; similar materials together make for easier separation and recycling; there are many types of ceramics, polymers etc.

A.2 Quick questions (page 479)

1. the Mn^{2+} ion has unpaired electrons and hence will exhibit paramagnetism: attraction to an applied magnet; Zn^{2+} has all electrons paired and will exhibit diamagnetism, so it will be weakly repelled by a magnet.
2. 0.79 g Cu metal

Questions (page 483)

1. a) positive argon gas ions and negative electrons
b) (i) testing samples produced by successive dilution of a solution of a particular magnesium compound with an accurately known concentration;
(ii) $1000\text{mg} = 1\text{g} = 1/24.5 \text{ mol Mg}$; this is a concentration of about .05M, thus the concentration of Mg would be beyond the scope of this curve and it is not very useful;
(iii) MS separates out by mass; OES would give a different emission spectrum for Mn^+ than Mg^{2+} ; relative abundance could be determined by relative heights of peak in MS;

A.3 Questions (page 488)

- a) reduced costs and wastes due to small amounts; high surface area to volume ratio make them nearly as effective as homogenous catalysts;
- b) health concerns, as effects of nanoparticles is unknown;

A.5 Questions (page 500)

6. a) thermoplastics have cross-links held by intermolecular forces and can be melted and reformed; thermoset plastics are chemically bonded during formation and cannot be reformed;



- b) resin identification codes - ensures uniformity for recycling; addition - condensation - classification into similar reaction types / similar ways of bringing about reaction/production methods / predict possible monomers; flexible - brittle - direct towards appropriate uses;
- c) softens the plastic; separates the polymer chains / reduces intermolecular forces;
- d) all of the reagents end up in useful product; there is no chemical waste;
- e) hydrogen chloride/HCl/dioxin;

A.6 Questions (page 508)

5. mixture of carbon containing compound and inert diluant in gas/vapour phase, passed over a heated metal catalyst;
6. bi-molecular recognition is where molecules are selectively attached to specific surfaces, using hydrogen bonding, complementary based pairing, metal co-ordination, or other bonding system using chemical complements and structural compatibility; key components are chemical complements and structural compatibility; essential for bottom up molecular assembly because these molecules selectively attach to specific surfaces;
7. graphene and fullerene are sp^2 hybridized bonding, which has delocalized electrons; diamond is sp^3 hybridized with no delocalization of electrons for conductivity;

A.7 Questions (page 515)

1. a) atom economy is the number of atoms in the desired product/ number of atoms in reagents *100; as nearly all of the reagents end up in useful product, there is no waste in the production of PVC, so that is green; PVC is very difficult to recycle due to its strong bonds and has toxic effects on decomposition, releasing hydrogen chloride/HCl/dioxin making them very much not green;
b) A is from a C-Cl bond and B is from C-H bond; the plastic is most likely a PVC, with code RIC = 3; this is because all plastics contain C-H bonds, but the RIC code of 3 are the chlorinated plastics;
2. PCB has similar biological effects, but does not contain the center dioxin ring in its structure
3. atom economy is a measure of the mass of reactant molecules that end up in the desired product: $\% \text{ atom economy} = \frac{\text{molar mass of desired product}}{\text{molar mass of all reactants}} \times 100\%$ percent atom economy for N-methylphenylamine: $107/183 = 58.5\%$
4. the density of LDPE and HDPE is much too close to allow separation by this technique; too much inherent error involved;
5. carbon dioxide is a greenhouse gas/ CO_2 causes global warming, climate change *etc.*; produces toxic chlorine compounds/causes acid rain due to HCl;
6. difficulties: energy intensive, difficult to separate, cannot be re-used in plastics involved in food contact; may contain halogens (such as bromine or chlorine), the recycling consumes a lot of energy in the crushing, washing, re-fabrication processes, not all plastics can be recycled;
advantages: less petroleum needed to be refined into plastics, less landfill space, as plastics do not decompose easily, less plastic likely to end up in the pacific gyre, considered socially responsible for the global environment, reduction of harmful emissions/ recycling does not produce the same greenhouse gases as manufacturing, less use of metal catalysts;

A.8 Quick question (page 522)

FCC

Questions (page 525)

1. a) BCC; co-ordination number = 8; 2 atoms per unit cell
b) (i) $n\lambda = 2d\sin\phi$; $d = n\lambda/(2\sin\theta) = 154/(2\sin 14.17) = 314.5\text{pm}$
(ii) volume = $l \times w \times h = (3.145 \times 10^{-10} \text{ m})^3 = 3.11 \times 10^{-29} \text{ m}^3 = 3.11 \times 10^{-23} \text{ cm}^3$



$$\text{(iii) density} = \frac{\text{no atoms per unit cell} \times \text{mass of Nb atom}}{(\text{volume of cell} \times N_a)}$$

$$\text{Nb density} = 2 \times 92.91 / ((3.11 \times 10^{-23}) \times 6.02 \times 10^{23}) = 9.92 \text{ g cm}^{-3}$$

$$\text{(iv) for BCC, } r = L \times \sqrt{\frac{3}{4}}; 314.5 \text{ pm} \times \sqrt{\frac{3}{4}} = 136 \text{ pm}; \text{ atomic radii depends on the context}$$

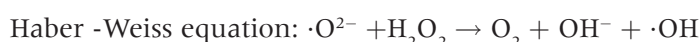
- c) (i) diamagnetic compounds have all electron spins paired and are weakly repelled by magnetic fields, while paramagnetic materials have electrons which are not paired and are attracted by magnetic fields; niobium will be paramagnetic as electrons are not paired;
- (ii) graph should have magnetic field as y axis and Kelvin temperature as x axis; it should show a sharp transition to zero resistance, with no mixed range; type 2 semiconductors have a gradual transition of mixed superconducting and normal behaviour;
- (iii) at low temperatures, the positive ions in the lattice are attracted to a passing electron, distorting the lattice slightly; a second electron is attracted to this slight positive deformation and a coupling of these two electrons occurs;
- (iv) a paradigm shift is a change in basic assumptions of a theory; type 1 superconductors do not show a gradual decrease of resistance and high temperature superconductors should have more collisions, hence more resistance; a change in view of how electrons move through materials (in a superconductor) could be viewed as an explanation, such as the theory of forming Cooper pairs;
2. a) smallest representative unit which when repeated in 3 dimensions generates the whole crystal
- b) X-ray crystallography
- c) planes of atoms diffract x-rays; interatomic distances can be calculated from wavelength of x-ray used; the diffraction pattern in conjunction with density information give information on the array, arrangement of these atoms in the crystal;
- d) R: $M = 8 \text{ corners} \times \frac{1}{8} \text{ atom/corner} + \text{centre atom} = 2$, $X = 6 \text{ face atoms} \times \frac{1}{2} \text{ atom per face} = 3$, therefore formula = M_2X_3
- Q: $M = 8 \text{ corners} \times \frac{1}{8} \text{ atom/corner} + 6 \text{ face atoms} \times \frac{1}{2} \text{ atom per face} = 4 \text{ ions/unit cell}$
 $X = 12 \text{ edges} \times \frac{1}{4} \text{ atom/edge} + \text{centre ion} = 4 \text{ ions/unit cell}$, therefore simplest formula is a 4:4 ratio (M_4X_4) or MX
3. a) monochromatic means all having the same frequency/wavelength; the angle of diffraction depends on the frequency/wavelength, so that, if the X-rays did not all have the same wavelength, there would not be a single diffraction angle;
- b) $n\lambda = 2d \sin\theta$; $d = n\lambda / (2\sin\theta) = 1 \times 154 / (2 \sin 15.5) = 288 \text{ pm}$
- c) (i) $8 \times \frac{1}{8} + 1 \text{ centre} = 2 \text{ atoms/unit cell}$
- (ii) volume of one mole of Cr is $6.02 \times 10^{23} \times \frac{1}{2} \times (288 \times 10^{-12} \text{ m}) = 7.19 \times 10^{-6} \text{ m}^3$
density = $m/V = 52.00 / 7.19 \times 10^{-6} = 7.23 \times 10^6 \text{ g m}^{-3} = 7.23 \text{ g cm}^{-3}$
- d) (i) solid
- (ii) hydrogen; their electron density is too low;
- (iii) the electron density is quite high indicating covalent bonding
4. see figure 8 on page 520
5. a) 11.33°
- b) FCC
6. see figure 1 on page 516 for graph of conductor and figure 2 on page 517 for resistance vs temperature graph of a typical superconductor;
7. above T_c is graph b; below T_c is graph c; mixed transition state is graph a;



8.	Element	Density (g cm ⁻³)	Length of cubic crystal edge (pm)	Radius of atom from X-ray diffraction data (pm)	Crystal type
	Iron, Fe	7.87 g/cm ³	287 pm	125 pm	BCC
	Sodium	.968 g/cm ³	429 pm	154 pm	BCC
	Platinum	21.09 g/cm ³	394 pm	139 pm	FCC

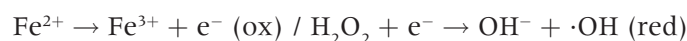
A.10 Questions (page 538)

1. a) application of Hess's law

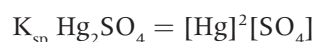


- b) must be homogeneous as it is *in vivo*/ ionic /intracellular

- c) $\text{Fe}^{3+} + \text{e}^- \rightarrow \text{Fe}^{2+}$ (reduction)/ $\text{O}_2^- \rightarrow \text{O}_2 + \text{e}^-$ (ox)



2. a) $[\text{Hg}] = 3 \times 10^{-6}$



$$[\text{SO}_4] = 6.5 \times 10^{-7} / (3 \times 10^{-6})^2 = 7.2 \times 10^4 \text{M}$$

- b) 10^4 M is ridiculously high, not a means which would work; use carbonate (K_{sp} in a reasonable range for Hg_2CO_3) or scrubbing, chelating, or other effective means;

- b) $K_{\text{sp}} = [\text{Mg}^{2+}] \cdot [\text{OH}^-]^2$

$$[\text{Mg}^{2+}] = \frac{1}{4} \times 1.20 \times 10^{-11}$$

$$[\text{Mg}^{2+}] = 3.00 \times 10^{-10} \text{ mol dm}^{-3}$$

3. $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}_{(\text{aq})} + \text{EDTA}^{4-}_{(\text{aq})} \rightarrow [\text{Cr}(\text{EDTA})]^{-}_{(\text{aq})} + 6\text{H}_2\text{O}_{(\text{l})}$; increase in entropy as a result of releasing 6 smaller molecules helps drive the reaction;

4. precipitant reacts with anion to create insoluble salt which can be removed as sludge; chelation forms a complex ion with two or more co-ordinate/dative bonds so that the metal will not bond with other substances, such as a protein, the complex ion can be secreted; absorption used in waste water treatment as part of filtration;

5. $K_{\text{sp}} \text{Zn}(\text{OH})_2 = 3 \times 10^{-17} \text{ Sol. Zn} = 3 \times 10^{-11} \text{M}$; at pH 3 $[\text{OH}^-]$ greatly reduced, therefore $[\text{Zn}]$ increased.



Option B - Biochemistry

B.1 Questions (page 546)

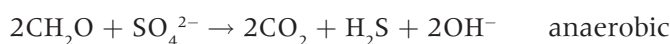
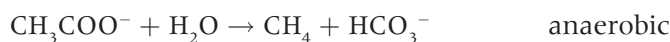
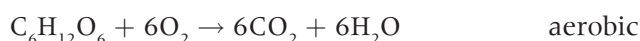
1. see side box on page 540
2. proteins (peptides/polypeptides), sugars (carbohydrates)
- 3.

Difference	Metabolic reactions	Traditional organic reactions
Efficiency/yield	Often proceed quantitatively (have nearly 100% yields)	Yields are usually lower than 100%
Reaction rate/time	Usually very fast (short reaction times)	Usually slow (long reaction times)
Reaction conditions	Ambient conditions (body temperature and normal pressure)	Often require high temperatures and sometimes high pressures
Solvent/medium	Water (aqueous environment)	Organic solvents (water-free environment)
Catalyst	Enzymes	Simple inorganic or organic molecules or no catalyst

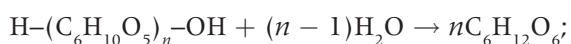
4. increase in the oxidation number
5. see side box at the bottom of page 542
6. $2\text{HSCH}_2\text{CH}(\text{NH}_2)\text{COOH} \rightarrow \text{HOOCCH}(\text{NH}_2)\text{CH}_2\text{S}-\text{SCH}_2\text{CH}(\text{NH}_2)\text{COOH} + 2[\text{H}]$
hydrogen atoms are lost, hence oxidation
7. see side box on page 543
8. photosynthesis transforms light energy into chemical energy; photons absorbed by chlorophyll in the cells of plants and certain bacteria are used as the source of energy for a series of anabolic reactions that ultimately lead to the oxidation of water, reduction of carbon dioxide, and the synthesis of energy-rich organic molecules;
9. a) carbon dioxide
b) water
c) water and carbon dioxide (some oxygen atoms from water are released to the atmosphere as oxygen gas while other oxygen atoms from water and nearly all oxygen atoms from carbon dioxide are used in the biosynthesis of organic molecules);
10. $6\text{CO}_2 + 6\text{H}_2\text{O} \xrightarrow{\text{light}} \text{C}_6\text{H}_{12}\text{O}_6 + 6\text{O}_2$
 $M(\text{C}_6\text{H}_{12}\text{O}_6) = 6 \times 12.01 + 12 \times 1.01 + 6 \times 16.00 = 180.18 \text{ g mol}^{-1}$
 $n(\text{C}_6\text{H}_{12}\text{O}_6) = 3.15/180.18 = 0.0175 \text{ mol}$
 $n(\text{CO}_2) = 6 \times 0.0175 = 0.105 \text{ mol}$
 $M(\text{CO}_2) = 12.01 + 2 \times 16.00 = 44.01 \text{ g mol}^{-1}$
 $m(\text{CO}_2) = 44.01 \times 0.105 = 4.62 \text{ g}$
11. no definite answer is possible, but responses can include the following: yes, as a single bacterial cell can usually produce a broader range of organic molecules than any single cell of our body; no, as humans are multicellular organisms, and the total number of different molecules produced in our bodies is greater than that produced by any single bacteria; yes, as bacteria can indeed produce copies of themselves from inorganic materials only; no, as the structure of any given bacteria is simpler than that of the human body; metabolic reactions in all living organisms are very similar, often catalysed by the same enzymes, and proceed in the same types of cellular tissues, so the existing differences in their metabolisms are negligible;



12. aerobic reactions often involve molecular oxygen (O_2), while anaerobic reactions often produce molecules with low oxidation states of carbon (CH_4), sulfur (H_2S) and other non-hydrogen atoms, therefore:



13. in biochemistry, hydrolysis reactions involve water molecules as reactants and typically produce two or more products from a single substrate (which is often a biopolymer), for example:



in contrast, condensation reactions release molecule(s) of water as product(s) and produce a single product (often a biopolymer) from two or more organic reactants (substrates) – an example is given in the next answer;

14. $6C_6H_{12}O_6 \rightarrow H-(C_6H_{10}O_5)_6-OH + 5H_2O$ (condensation)

15. $M[H-(C_6H_{10}O_5)_6-OH] = 36 \times 12.01 + 62 \times 1.01 + 31 \times 16.00 = 990.98 \text{ g mol}^{-1}$

$$n[H-(C_6H_{10}O_5)_6-OH] = 4.95/990.98 = 0.00500 \text{ mol}$$

$$n(H_2O) = 5 \times 0.00500 = 0.0250 \text{ mol}$$

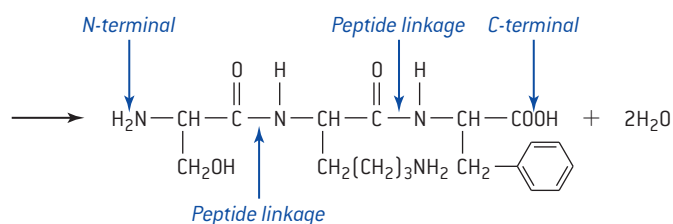
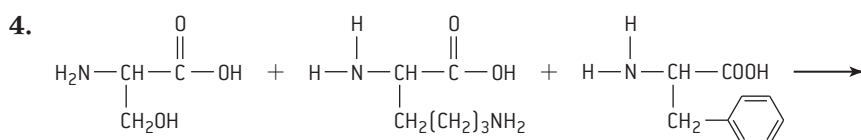
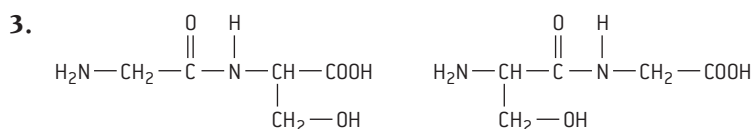
$$M(H_2O) = 2 \times 1.01 + 16.00 = 18.02 \text{ g mol}^{-1}$$

$$m(H_2O) = 18.02 \times 0.0250 = 0.451 \text{ g}$$

B.2 Questions (page 563)

1. a) (i) $\begin{array}{c} \text{H}_3\text{N}^+ - \text{CH} - \text{COOH} \\ | \\ \text{CH}_2 - \text{OH} \end{array}$ (ii) $\begin{array}{c} \text{H}_2\text{N} - \text{CH} - \text{COO}^- \\ | \\ \text{CH}_2 - \text{OH} \end{array}$ b) $\begin{array}{c} \text{H}_3\text{N}^+ - \text{CH} - \text{COO}^- \\ | \\ \text{CH}_2 - \text{OH} \end{array}$

2. they have one or more ionic centres and at least two polar functional groups; these centres and groups can form multiple ion-dipole, dipole-dipole and hydrogen bonds with water, hence 2-amino acids are readily soluble in water; in solid amino acids, the same groups form multiple intermolecular bonds, including ionic, ion-dipole, dipole-dipole and hydrogen bonds; breaking these bonds requires a lot of energy and therefore can occur only at high temperatures, hence 2-amino acids have high melting points;



5. primary structure is the sequence (order) of amino acids; secondary structure is the regular (repeating) folding and/or coiling of amino acid chains (such as α -helix or β -pleated sheet); primary structure is maintained by covalent (peptide) bonds; secondary structure is maintained by hydrogen bonds;



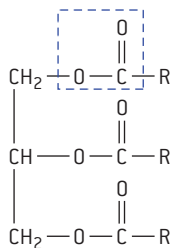
6. the five most common interactions are: (1) van der Waals' attraction between two non-polar groups (such as CH_3 , C_6H_5 , etc.); (2) ionic bonding between charged groups (such as NH_3^+ and COO^-); (3) hydrogen bonding between H bonded to O or N atom with another O or N atom; (4) disulfide bridges (bonds) between two S atoms (occur between cysteine side chains); (5) peptide linkages (bonds) between $-\text{COOH}$ and $-\text{NH}_2$ groups; other interactions (such as ester bonds between $-\text{COOH}$ and $-\text{OH}$ groups) are also possible;
7. **a)** Trp and Leu: van der Waals' forces (other acceptable answers include London forces, dispersion forces, temporary/induced dipole-dipole interactions);
Cys and Cys: disulfide bridges (i.e., covalent bond between S atoms);
Tyr and His: hydrogen bonding;
b) refer to answer 6
8. structure/growth/tissue repair; enzymes/biological catalysts; hormones/chemical messengers/metabolism regulators; transport/carriers of other molecules; immunoproteins/antibodies; source of energy and 2-amino acids;
9. the quaternary structure of proteins is maintained by predominantly non-covalent interactions between separate polypeptide chains (protein molecules)
10. **a)** peptide (amide) linkage, $-\text{C}(\text{O})-\text{NH}-$
b) refer to page 551
11. **a)** qualitative: identification of an unknown substances, verification of the purity of a substance, determination of the qualitative composition of a mixture; quantitative: measurement of the concentration/amount of a substance in a solution, mixture or biological material; determination of the ratio of components in a mixture (i.e., qualitative composition of the mixture); determination of an R_f value of a component;
b) components dissolve in the mobile phase (any appropriate solvent) and adsorb onto the stationary phase (usually silica or alumina); different components have different solubilities in the mobile phase and different affinities for the stationary phase, therefore they distribute/partition between the stationary and mobile phases in different proportions; components move only when they are in the mobile phase; better soluble and/or less adsorbed components elute earlier (leave the column first);
12. R_f of a substance is the ratio of the distance travelled by the spot of this substance on a chromatogram to the distance travelled by the solvent front; the R_f value of a given substance does not depend on the absolute distances travelled by its spot and the solvent front but depends on all other experimental conditions, such as the solvent(s) used, paper type, temperature and pH of the solution;
13. $R_{f1} = L_1/L_0 = 10/70 \approx 0.14$ (lysine)
 $R_{f2} = L_2/L_0 = 28/70 \approx 0.40$ (cysteine)
 $R_{f3} = L_3/L_0 = 35/70 = 0.50$ (asparagine)
14. **a)** refer to page 552
b) provides more efficient and/or faster separation of components; components can be easily recovered or detected; some stationary phases in TLC can withstand strong solvents, acids and bases;
c) $R_f = 40/46 = 0.87$ (please note that R_f is unitless)
15. refer to pages 551 and 552
16. possible responses can include the following:

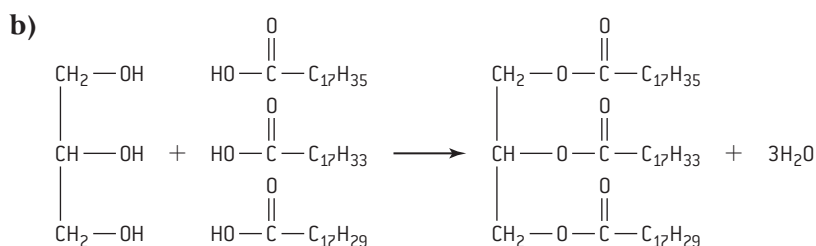


Traditional catalyst	Enzyme
Simple organic or inorganic molecules, such as acids, bases, metal ions or complexes	Very large organic molecules, usually proteins or other biopolymers
Limited efficiency	Very high efficiency
Usually non-specific (i.e., can catalyse various reaction types)	Highly specific (can catalyse one or few reactions)
Temperature and pH usually have little effects on the catalytic activity	Catalytic activity is strongly affected by temperature and pH
Can be poisoned (deactivated) by various inorganic or organic molecules and/or ions	Can be inhibited (reversibly or irreversibly) by specific organic molecules
Can be heterogeneous or homogeneous	Always homogeneous
Both accelerate chemical reactions by providing alternative reaction pathways with lowered activation energy.	

17. no, as the enzyme will become saturated and the reaction rate will not depend on the substrate concentration (i.e., the first-order reaction will become the zero-order reaction); refer to pages 612 and 613 for a more detailed explanation;
18. a) each enzyme has an active site (or sites) where a substrate can bind; this process is described by the “lock and key” and “induced fit” models (refer to pages 561 and 611); enzyme–substrate interactions weaken chemical bonds and lower the activation energy of the reaction by providing an alternative reaction pathway;
- b) increasing temperature initially increases the reaction rate because at higher temperatures more molecules possess energies equal or greater than the activation energy; for a typical enzyme, the highest reaction rate is achieved at around 37°C; above 40°C, many enzymes undergo denaturation due to changes in their tertiary structures and therefore the shapes of their active sites; such changes decrease the enzyme activity and lower the reaction rate; at 60°C, most enzymes completely lose their catalytic activity, which reduces the reaction rate to zero;

B.3 Questions (page 578)

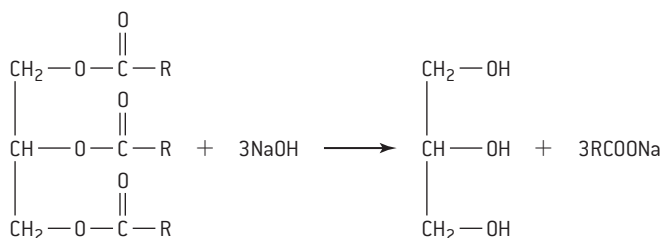
1. a) the mass of iodine that reacts with 100 g of the unsaturated compound (fat, oil, lipid, etc.)
 b) $n(\text{linoleic acid}) = 1.00/281 = 0.00356 \text{ mol}$
 $n(\text{I}_2) = n(\text{double bonds}) = 2 \times 0.00356 = 0.00712 \text{ mol}$
 $V(\text{I}_2 \text{ solution}) = 0.00712 \text{ mol}/1.00 \text{ mol dm}^{-3} = 0.00712 \text{ dm}^3 = 7.12 \text{ cm}^3$
2. a) $\text{C}_{19}\text{H}_{39}\text{COOH}$: none; $\text{C}_{19}\text{H}_{31}\text{COOH}$: four; $\text{C}_{19}\text{H}_{29}\text{COOH}$: five;
 b) $\text{C}_{19}\text{H}_{29}\text{COOH}$, as it has the greatest number of C=C bonds (most unsaturated); the higher the number of carbon–carbon double bonds, the lower the stability of the acid to oxidation, light, heat, moisture and enzymes;
3. 
4. a) saturated: stearic ($\text{C}_{17}\text{H}_{35}\text{COOH}$); monounsaturated: oleic ($\text{C}_{17}\text{H}_{33}\text{COOH}$); polyunsaturated: linolenic ($\text{C}_{17}\text{H}_{29}\text{COOH}$);



c) phospholipids and steroids;

d) the response can include the following: all three types of lipids are predominantly hydrophobic (non-polar) as they contain mostly hydrocarbon fragments; triglycerides and most phospholipids contain a fragment of glycerol; steroids are polycyclic compounds (contain several rings); phospholipids contain phosphate group(s); triglycerides and phospholipids are esters;

5. saponification of a triglyceride proceeds as follows:



therefore, 5.0 moles of a triglyceride will react with $3 \times 5.0 = 15$ moles of NaOH

$$M(\text{NaOH}) = 22.99 + 16.00 + 1.01 = 40.00 \text{ g mol}^{-1}$$

$$m(\text{NaOH}) = 15 \times 40.00 = 600 \text{ g}$$

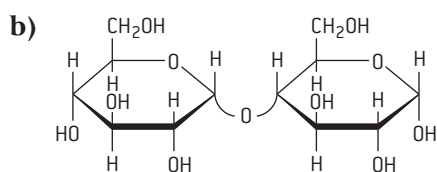
6. a) because fats are less oxidized (contain fewer oxygen atoms) than carbohydrates and therefore can release more energy during complete oxidation
- b) the presence of C=C bonds in linoleic acid produce kinks in the hydrocarbon chain; kinked chains cannot pack as closely as more regular chains in stearic acid; larger distances between chains lead to weaker van der Waals' (London/intermolecular/dispersion) forces in linoleic acid and therefore reduce its melting point;
7. a) all these acids are saturated, so their melting points will depend on the number of electrons in their molecules; stearic acid has the longest hydrocarbon chain and therefore will have the highest melting point;
- b) the molecules of fatty acids in the second group are unsaturated, have similar sizes and therefore similar numbers of electrons; in such case, the melting points will depend on the degree of unsaturation (each additional C=C bond will decrease the melting point, as it was explained in the previous answer); therefore, oleic acid (containing only one C=C bond) will have the highest melting point;
8. a) to prevent chocolate from melting, fats with higher melting points must be used in hot climates
- b) in a hot climate, the chocolate must contain more saturated (hydrogenated) fats, fats with longer hydrocarbon chains, or fats with *trans*-configuration of C=C bonds (*trans*-fats); such fats are more crystalline (have relatively high melting points);
9. a) unpleasant smell, taste, texture and/or appearance;
- b) hydrolytic rancidity: lipids are converted into glycerol and fatty acids (this process requires water and enzymes); oxidative rancidity: in the fragments of unsaturated fatty acids, the C=C bonds undergo oxidation, usually by molecular oxygen (this process can be also catalysed by enzymes);



10. a) double carbon-carbon bond(s)
 b) rancid (due to the process of oxidative rancidity)
 c) light produces free radicals by homolytic fission (breaking) of chemical bonds
 d) phenol groups (the C_6H_5-OH fragments)
11. $\text{heat} = (m \times C \times \Delta T)_{\text{water}} + (C \times \Delta T)_{\text{glass}} = 100.00 \times 4.18 \times 9.4 + 90.2 \times 9.4 \approx 4800 \text{ J} = 4.8 \text{ kJ}$
 energy value = $4.8 \times 100/5.00 = 96 \text{ kJ}$
12. possible responses can include the following: labelling and safety regulations vary between countries; a food product may be considered safe in one country and toxic in another country; toxic or otherwise harmful components of food (such as colourants, preservative, etc.) may not be banned in all countries;
13. possible responses can include the following: individuals have rights to make choices about their diet; poor dietary choices of individuals negatively affect the entire society (by increasing the cost of health and social services, reducing the productivity of workforce and therefore the taxes collected by the government, etc.); children must be protected by the society from inadequate dietary choices made by their parents (e.g., whether strict vegan diet is suitable for very young children); certain foods are socially unacceptable (e.g., made of pets, primates, endangered species, involving cruel treatment of animals, etc.);
- 14.
- $$\begin{array}{c}
 \text{CH}_2-\text{O}-\overset{\text{O}}{\parallel}{\text{C}}-\text{C}_{15}\text{H}_{31} \\
 | \\
 \text{CH}-\text{O}-\overset{\text{O}}{\parallel}{\text{C}}-\text{C}_{17}\text{H}_{31} \\
 | \\
 \text{CH}_2-\text{O}-\overset{\text{O}}{\parallel}{\text{P}}-\text{OH} \\
 | \\
 \text{OH}
 \end{array}
 + 5\text{NaOH} \longrightarrow
 \begin{array}{c}
 \text{CH}_2-\text{OH} \\
 | \\
 \text{CH}-\text{OH} \\
 | \\
 \text{CH}_2-\text{OH}
 \end{array}
 + \begin{array}{c} \text{C}_{15}\text{H}_{31}\text{COONa} \\ \text{C}_{17}\text{H}_{31}\text{COONa} \\ \text{Na}_3\text{PO}_4 \end{array}
 + 2\text{H}_2\text{O}$$
15. a) steroidal backbone (four hydrocarbon rings)
 b) phospholipids and triglycerides
 c) high density lipoprotein and low density lipoprotein
 d) HDLs have higher proportion of protein units and lower proportion of lipid units than LDLs
 e) LDLs can be retained in the arteries and block them by initiating the formation of plaque(s); this increases the risk of atherosclerosis (heart disease)
16. a) a chemical messenger produced in a gland and transported through the blood to the site of action
 b) 21
17. a) dianabol contains an extra methyl ($-\text{CH}_3$) group and an extra carbon-carbon double bond ($\text{C}=\text{C}$), so dianabol is more unsaturated and contains larger system of electron conjugation than testosterone; dianabol is a tertiary alcohol while testosterone is a secondary alcohol;
 b) refer to answer 16
 c) because dianabol is structurally similar to progesterone and estradiol, which are female sex hormones;

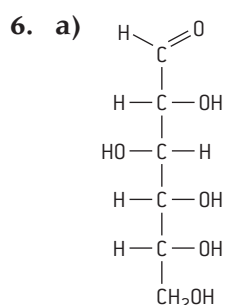
B.4 Questions (page 589)

1. a) $\Delta T = 27.55 - 20.20 = 7.35 \text{ K}$
 $\text{heat} = m \times C \times \Delta T = 200.10 \text{ g} \times 4.18 \text{ J g}^{-1} \text{ K}^{-1} \times 7.35 \text{ K} = 6.15 \times 10^3 \text{ J}$
 energy value = $6.15 \times 10^3 \text{ J} / 0.395 \text{ g} \approx 15.6 \times 10^3 \text{ J g}^{-1}$

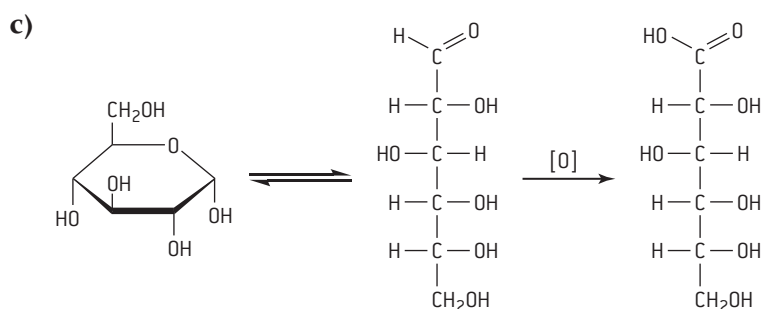


c) energy reserve/building block for other biologically important molecules

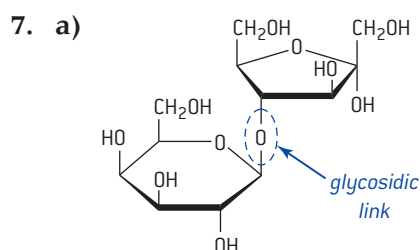
2. all contain one carbonyl ($\text{C}=\text{O}$) group; all contain at least two hydroxyl ($-\text{OH}$) groups; most monosaccharides have the empirical formula CH_2O ;
3. a) an aldose contains an aldehyde group (i.e., a carbonyl group at the terminal carbon atom); a ketose contains a ketone group (i.e., a carbonyl group at a non-terminal carbon atom);
 b) similarity: both contain five carbon atoms; difference: aldopentose contains a carbonyl group at the terminal carbon atom while ketopentose contains a carbonyl group at a non-terminal (usually the second) carbon atom;
 c) aldose and hexose, or aldohexose;
4. all monosaccharides contain hydroxyl ($-\text{OH}$) and carbonyl ($\text{C}=\text{O}$) groups; these groups form multiple hydrogen bonds with water molecules, hence all monosaccharides are soluble in water;
5. a) aldehyde (i.e., carbonyl group at the terminal carbon atom, $-\text{CHO}$)
 b) ketone (i.e., carbonyl group at the second carbon atom, $-\text{C}(\text{O})-$)
 c) glucose



b) aldehyde (i.e., carbonyl group at the terminal carbon atom)



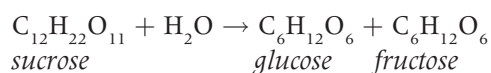
d) sucrose





- b) lactulose is a reducing sugar; the five-membered ring in lactulose has a free glycosidic OH group and therefore can undergo ring-chain tautomerism, producing an open-chain ketose; under alkaline conditions, this ketose can isomerize into aldose, which will give positive tests with both Fehling's and Benedict's reagents (as both tests require the presence of a base);

8. acid catalyses the hydrolysis of sucrose into glucose and fructose:



fructose is much sweeter than sucrose, hence the taste becomes stronger;

9. a) glycerol has hydroxyl (–OH) groups, which can participate in condensation reactions with fatty acids; such condensation reactions are also known as esterification and nucleophilic substitution;
- b) lactose also has hydroxyl groups, which react with fatty acids in the same way as hydroxyl groups in glycerol
- c) lactose is larger than glycerol and has more hydroxyl groups, so it can esterify greater number of fatty acids; if large fatty acids were used in such reaction, the product would have very high melting point; in contrast, short hydrocarbon chains of fatty acids in olestra reduce its melting point and produce a substance similar to traditional cooking fats;

10. amylose and amylopectin;

B.5 Questions (page 596)

1. both vitamin A and D are predominantly non-polar, readily soluble in fats and almost insoluble in water;
2. a) vitamin B3: carboxyl group (–COOH) and amino group (heterocyclic nitrogen atom, =N–); vitamin E: phenolic hydroxyl group (–OH) and ether group (heterocyclic oxygen atom, –O–); in both cases, aromatic rings (six-membered rings with alternating single and double bonds) can be also considered as functional groups;
- b) phenolic hydroxyl group (–OH) and quaternary carbon atom (next to oxygen in the six-membered ring);
- c) vitamin B3: small polar molecule, capable of forming ions and multiple hydrogen bonds with water molecules, hence soluble in water and insoluble in fats; vitamin E: only one polar group (–OH) but very long non-polar hydrocarbon chain, hence this molecule is predominantly non-polar, soluble in fats and insoluble in water;
- d) vitamin B3 is water soluble, so it concentrates in the blood plasma, excretes quickly and therefore must be ingested regularly; vitamin E is fat soluble, so it accumulates in fatty tissues and can be stored in the human body for a long time; this vitamin can be taken less regularly without any detrimental health effects;
3. $\text{C}_6\text{H}_8\text{O}_6 \rightarrow \text{C}_6\text{H}_6\text{O}_6 + 2\text{H}^+ + 2\text{e}^-$
4. a) hydroxyl group
- b) the molecular formulae of vitamin C and glucose are $\text{C}_6\text{H}_8\text{O}_6$ and $\text{C}_6\text{H}_{12}\text{O}_6$, respectively; since vitamin C contains fewer hydrogen atoms (8) than glucose (12), it is less reduced (more oxidized) and therefore will release less energy during complete oxidation; thus, the dietary energy value of vitamin C will be lower than that of glucose;
5. a) vitamin D
- b) the response can include the following: yes, as the synthesis of vitamin D in the human body requires sunlight, which might be unavailable for prolonged periods of time in certain parts of the world (e.g., in northern countries during the winter) or inefficient due to modern lifestyles

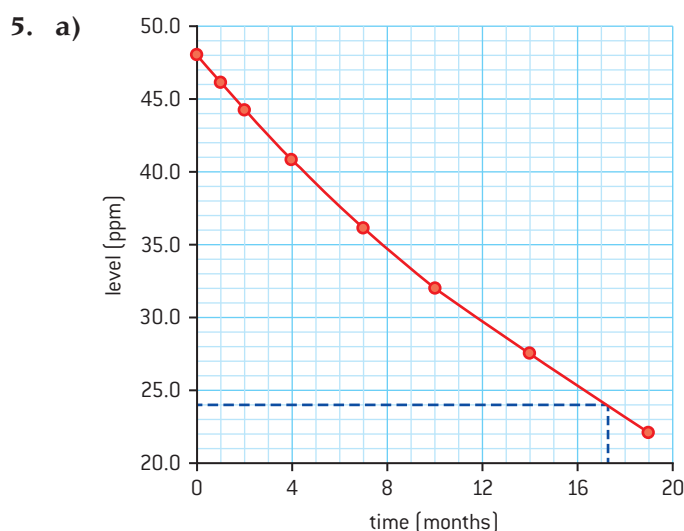


and the use of sunscreen; no, as the above issues can be resolved by increased exposure to natural or artificial light; yes, as the lack or deficiency of vitamin D produces characteristic health conditions, which is typical for essential micronutrients; no, as vitamin D does match exactly the definition of an essential micronutrient; yes, as vitamin D is traditionally classified as vitamin;

6. refer to answer 5 (b)
7. the response can include the following: vitamin supplements; changes in diet; food fortification; reduction in smoking and alcohol consumption (to prevent secondary deficiencies);
8. the response can include the following: (i) for advantages—increased nutritional value of common dietary products; prevention of widespread deficiencies (caused by geological or cultural factors); benefits to local and global economy (lower cost of health service, increased productivity of workforce, etc.); (ii) for disadvantages—freedom of people to make dietary choices; possibility of allergic reactions and vitamin poisoning; increased cost of food;

B.6 Questions (page 605)

1. $3.3 \text{ ng m}^{-3} = 3.3 \times 10^{-9} \text{ g m}^{-3} = 3.3 \times 10^{-15} \text{ g cm}^{-3}$
 $c(\text{PCB}) = 6.02 \times 10^{23} \text{ mol}^{-1} \times 3.3 \times 10^{-15} \text{ g cm}^{-3} / 320 \text{ g mol}^{-1} \approx 6.2 \times 10^6 \text{ cm}^{-3}$
 since PCBs are molecular compounds, the units “ cm^{-3} ” mean “molecules of PCB per cm^3 ”
2. refer to page 599
3. over 5 years, or $5 \times 365.25 \approx 1826$ days, the bear will consume $10 \times 1826 = 18260 \text{ kg}$ of fish; the mass of the pollutant in the consumed fish will be $18260 \text{ kg} \times 2 \times 10^{-6} \% / 100 \% \approx 3.65 \times 10^{-4} \text{ kg}$, which will constitute $(3.65 \times 10^{-4} \text{ kg} / 600 \text{ kg}) \times 100 \% \approx 6 \times 10^{-5} \%$ of the bear's body; due to biomagnification, this value is 30 times higher than the pollutant level in the fish;
4. refer to page 598



- b) the half-life of DDT is approximately 17.2 months (during this time, the level falls from 48.0 to 24.0 ppm, as shown by the red dotted line on the plot);
- c) since the level of DDT halves every 17.2 months, we can draw the following table (1 ppm = 1000 ppb):

Time(months)	DDT level (ppb)	Time(months)	DDT level (ppb)	Time(months)	DDT level (ppb)
0	48000	137.6	188	275.2	0.73
17.2	24000	154.8	94	292.4	0.37
34.4	12000	172.0	47	309.6	0.18
51.6	6000	189.2	23	326.8	0.092
68.8	3000	206.4	12	344.0	0.046
86.0	1500	223.6	5.9	361.2	0.023
103.2	750	240.8	2.9	378.4	0.011
120.4	375	258.0	1.5	395.6	0.006

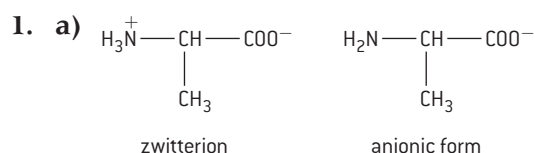
therefore, it will take approximately 385 months, or $385 / 12 = 32$ years before the level of DDT falls below 0.01 ppb; if the field was treated with DDT in 1970, this insecticide could still be detected in the soil in the beginning of the 21st century;

6. refer to page 601
7. multiple non-covalent interactions, including van der Waals' forces, ionic and hydrogen bonds;
8. a) refer to page 603
b) assuming that the target product is dimethyl carbonate, atom efficiency will be:

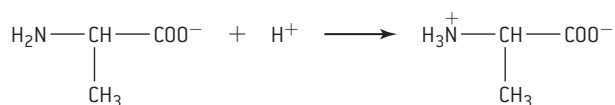
$$\frac{2M_r(\text{dimethyl carbonate})}{4M_r(\text{CH}_3\text{OH}) + 2M_r(\text{CO}) + M_r(\text{O}_2)} = \frac{2 \times 90.09}{4 \times 32.05 + 2 \times 28.01 + 32.00} \approx 0.833 = 83.3\%$$

- possible responses can include the following: ethanoic acid is a common metabolite, which is readily biodegradable; neutralisation reactions involving ethanoic acid usually proceed less vigorously than similar reactions with sulfuric acid; concentrated ethanoic acid is a weaker dehydrating agent than concentrated sulfuric acid, so it is less likely to cause severe damage to personnel or produce fire in contact with certain materials; ethanoic acid is more expensive than sulfuric acid; ethanoic acid is monobasic acid while sulfuric acid is dibasic (so more ethanoic acid is needed to neutralise the same quantity of alkaline waste); in contrast to sulfuric acid, pure ethanoic acid is flammable and volatile, has unpleasant smell and is toxic if inhaled; ethanoic acid is weak, so the neutralization of alkaline waste with ethanoic acid might produce a slightly alkaline solution (due to the hydrolysis of the resulting salts); in contrast to sulfates, all acetates are soluble (which might be both an advantage or a disadvantage, depending on the waste composition and the purpose of its neutralisation);

B.7 Questions (page 617)



- b) reaction with a strong acid:**



reaction with a strong base:





2. a) original solution:

$$n(\text{HCl}) = 0.60 \text{ dm}^3 \times 0.20 \text{ mol dm}^{-3} = 0.12 \text{ mol}$$

$$n(\text{glycine}) = 0.40 \text{ dm}^3 \times 0.50 \text{ mol dm}^{-3} = 0.20 \text{ mol}$$

since the densities of all solutions are 1.0 kg dm^{-3} , the total volumes of solutions are additive:

$$V(\text{buffer solution}) = 0.60 \text{ dm}^3 + 0.40 \text{ dm}^3 = 1.0 \text{ dm}^3$$

$$c(\text{HCl})_{\text{init}} = 0.12 \text{ mol} / 1.0 \text{ dm}^3 = 0.12 \text{ mol dm}^{-3}$$

$$c(\text{glycine})_{\text{init}} = 0.20 \text{ mol} / 1.0 \text{ dm}^3 = 0.20 \text{ mol dm}^{-3}$$

when the solutions were mixed, the following reaction occurred:

	$\text{H}_3\text{N}^+-\text{CH}_2-\text{COO}^- +$	$\text{H}^+ \rightarrow$	$\text{H}_3\text{N}^+-\text{CH}_2-\text{COOH}$
$c_{\text{init}} (\text{mol dm}^{-3})$	0.20	0.12	—
$\Delta c (\text{mol dm}^{-3})$	−0.12	−0.12	+0.12
$c_{\text{fin}} (\text{mol dm}^{-3})$	0.08	—	0.12

in this buffer solution, glycine exists as a mixture of zwitterions (conjugate base) and cations (conjugate acid), so the $\text{p}K_{\text{a}1}$ of glycine will be used in the Henderson–Hasselbalch equation; according to Table 1 on page 607, $\text{p}K_{\text{a}1}(\text{glycine}) = 2.3$, so:

$$\text{pH}_1 = \text{p}K_{\text{a}1} + \log \frac{[\text{zwitterion}]}{[\text{cation}]} = 2.3 + \log \frac{0.08}{0.12} = 2.12$$

b) $1.0 \text{ cm}^3 = 1.0 \times 10^{-3} \text{ dm}^3$, so $n(\text{HCl}) = 1.0 \times 10^{-3} \text{ dm}^3 \times 1.0 \text{ mol dm}^{-3} = 1.0 \times 10^{-3} \text{ mol}$

	$\text{H}_3\text{N}^+-\text{CH}_2-\text{COO}^- +$	$\text{H}^+ \rightarrow$	$\text{H}_3\text{N}^+-\text{CH}_2-\text{COOH}$
$c_{\text{init}} (\text{mol dm}^{-3})$	0.080	0.001	0.120
$\Delta c (\text{mol dm}^{-3})$	−0.001	−0.001	+0.001
$c_{\text{fin}} (\text{mol dm}^{-3})$	0.079	—	0.121

the qualitative composition of the buffer solution (zwitterions + cations) has not changed, so the same $\text{p}K_{\text{a}1}$ will be used:

$$\text{pH}_2 = \text{p}K_{\text{a}1} + \log \frac{[\text{zwitterion}]}{[\text{cation}]} = 2.3 + \log \frac{0.079}{0.121} = 2.11$$

as expected, the addition of a small quantity of HCl has barely affected the pH of the buffer solution

c) $n(\text{NaOH}) = 0.40 \text{ g} / 40.00 \text{ g mol}^{-1} = 0.010 \text{ mol}$

	$\text{H}_3\text{N}^+-\text{CH}_2-\text{COOH}$	$+ \text{OH}^- \rightarrow$	$\text{H}_3\text{N}^+-\text{CH}_2-\text{COO}^- + \text{H}_2\text{O}$
$c_{\text{init}} (\text{mol dm}^{-3})$	0.120	0.010	0.080
$\Delta c (\text{mol dm}^{-3})$	−0.010	−0.010	+0.010
$c_{\text{fin}} (\text{mol dm}^{-3})$	0.110	—	0.090

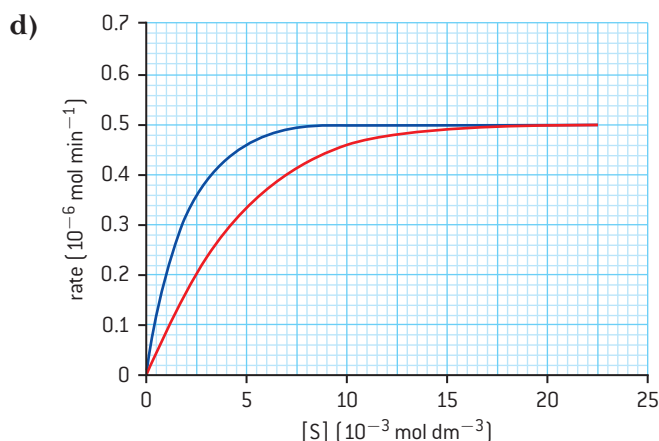
again, the qualitative composition of the buffer solution (zwitterions + cations) has not changed, so $\text{p}K_{\text{a}1}$ must still be used:

$$\text{pH}_3 = \text{p}K_{\text{a}1} + \log \frac{[\text{zwitterion}]}{[\text{cation}]} = 2.3 + \log \frac{0.090}{0.110} = 2.21$$

similar to the previous case, the addition of a small quantity of NaOH only slightly changes the pH of the buffer solution (from 2.12 to 2.21)



3. the response can include the following: both enzymes and inorganic catalysts increase rate of chemical reactions and reduce their activation energies by providing alternative reaction pathways; enzymes are more specific than inorganic catalysts; enzymes are easily denatured by changing conditions (temperature, pH, the presence of heavy metal ions, etc.); inorganic catalysts can be poisoned by certain substances and ions; enzymes can be inhibited by competitive and non-competitive inhibitors; enzymes have active sites that substrates bond to (“lock and key” and “induced fit” models); competitive inhibitors bond to active sites; non-competitive inhibitors bond to allosteric sites, which denatures enzymes by altering their shapes;
4. the response can include the following: both metaphors and models facilitate understanding by providing simple concepts and focussing our attention on the most important aspects of real objects or phenomena; both metaphors and models involve a certain degree of simplification, which distort our perception of real objects or phenomena; certain objects and phenomena (e.g., subatomic particles and quantum effects) cannot be observed or perceived directly and therefore can be understood only through the use of metaphors and models;
5. a) the response can include the following: most enzymes are proteins; the activity of each enzyme depends on its structure (tertiary and quaternary) and the nature of its active site; most enzymes can function only within narrow pH ranges; enzymes are denatured by heat while most inorganic catalysts can be used at high temperatures; also, refer to answer 3;
- b) the response can include the following: initial reaction rates are reduced in both cases; lead binds to the allosteric site of the enzyme (away from the active site) and changes the shape of the active site so the substrate no longer fits; ritonavir has a similar shape to the substrate and so binds to the active site instead of the substrate; lead lowers $V_{\max}$ but does not affect K_m ; ritonavir increases K_m but does not affect $V_{\max}$;
6. a) at low substrate concentrations, nearly all active sites are unoccupied, so the reaction rate is directly proportional to the substrate concentration (first-order reaction); at high substrate concentrations, nearly all active sites are occupied by substrates, so the rate reaches its maximum (zero-order reaction);
- b) competitive inhibitors occupy active sites and do not affect $V_{\max}$; non-competitive inhibitors bind to allosteric sites (away from active sites), which distorts the shapes of active sites and lowers $V_{\max}$;
- c) refer to figure 12 on page 562: the sketch must include a bell-shaped (or similar) curve and correctly labelled axes (pH on the X axis and rate or enzyme activity on the Y axis);
- d) the pH affects the charges on the amino acid residues in the enzyme. At higher or low pH, these charges change significantly, which alters the tertiary structure of the enzyme and the shape of its active site;
7. a) enzymes catalyse biochemical reactions;
- b) the shape of the active site depends on the tertiary and quaternary structures of the enzyme; when the substrate binds to the active site, some chemical bonds in the substrate break while new bonds form; as a result, the substrate is transformed into the product; the product is released from the active site, allowing another substrate molecule to bind;
- c) $V_{\max} = 0.50 \times 10^{-6} \text{ mol min}^{-1} = 5.0 \times 10^{-7} \text{ mol min}^{-1}$
 $K_m = [S] \text{ when } v = \frac{1}{2}V_{\max} = 1.4 \times 10^{-3} \text{ mol dm}^{-3}$



e) heavy-metal ions react irreversibly with $-SH$ groups by displacing the hydrogen atoms and forming strong covalent sulfur-metal bonds; this affects the shape of the enzyme and its active site, decreasing the enzyme activity and therefore the reaction rate; initially, an increase in temperature increases the enzyme activity and accelerates the reaction, as more reactant particles possess energy greater or equal to the activation energy; further increase in temperature (typically above $+40^{\circ}\text{C}$) denatures the enzyme and decreases the reaction rate; both heavy-metal ions and high temperature alters tertiary and quaternary structures of the enzyme and therefore the shape of its active site; these changes deactivate the enzyme;

8. a) non-competitive

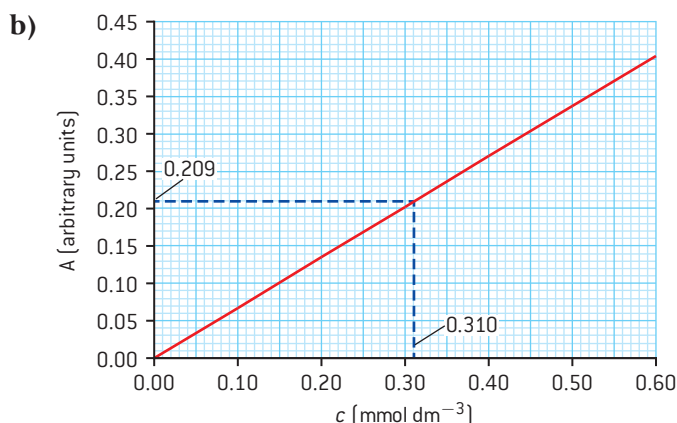
b) absence of the inhibitor: $V_{\max} = 4.4$, $K_m = 1.7$

presence of the inhibitor: $V_{\max} = 3.0$, $K_m = 1.7$

c) the higher the K_m value, the lower the enzyme activity

9. refer to page 615

10. a) aromatic rings in phenylalanine, tyrosine and tryptophan (without organic dyes) plus arginine side chains (in the presence of organic dyes);

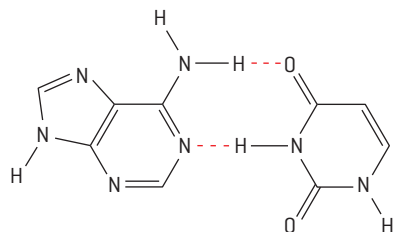


c) according to the calibration curve, the concentration of the protein in the analyzed (diluted) solution is $0.310 \text{ mmol dm}^{-3}$; the dilution increased the volume of the solution $25.0/2.00 = 12.5$ times, proportionally decreasing its concentration, therefore the concentration of the protein in the original solution was $12.5 \times 0.310 \text{ mmol dm}^{-3} \approx 3.88 \text{ mmol dm}^{-3}$;



B.8 Questions (page 628)

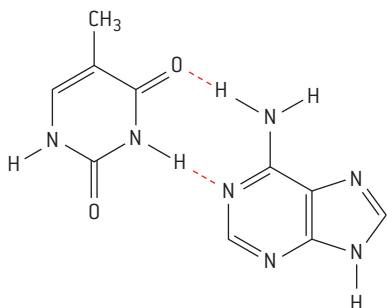
1.



hydrogen bonds are shown as red dashed lines

2. a) thymine is covalently bonded to deoxyribose via a condensation reaction; the reaction involves the NH group of thymine and the glycosidic OH group of the pentose sugar; as a result, the nitrogen atom of thymine becomes covalently bonded to the first carbon atom of deoxyribose;

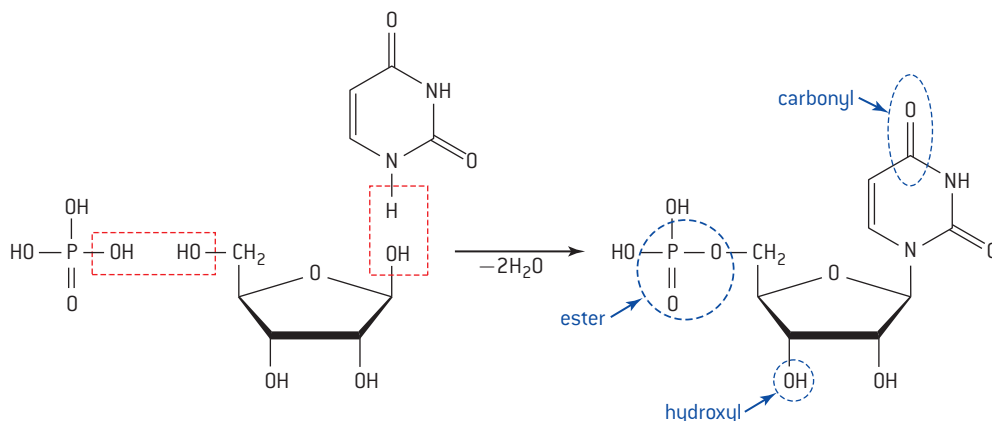
b)



two hydrogen bonds (red dashed lines) form between thymine (left) and adenine (right)

- c) each sequence of three bases represents one amino acid (triplet code); the triplet code allows for 64 permutations (codons); DNA is transcribed to RNA; the complete sequence for all bases is known as a genome;
- d) restriction enzymes break down the DNA into smaller fragments (minisatellites); splits occur in the regions where there are no codons; restriction enzymes have the ability to find a certain sequence of nucleotides; the different lengths of the sequences are unique to an individual;

3.



4. RNA contains fragments of ribose, DNA contains fragments of deoxyribose; RNA contains uracil, DNA contains thymine; RNA is usually single-stranded, DNA is usually double-stranded (forms double helix);
5. a) a DNA nucleotide contains a phosphate group, a pentose sugar (deoxyribose), and a nitrogenous base;
- b) they undergo condensation reactions where covalent bonds form between a phosphate group on one nucleotide and a pentose sugar on another;



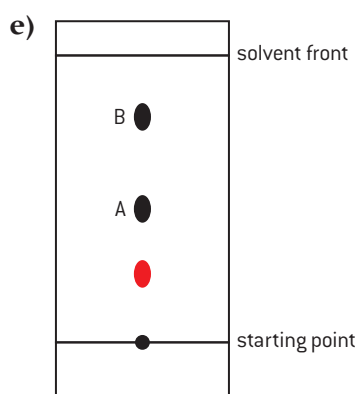
- c) DNA is separated from blood sample and cut into fragments (minisatellites) by restriction enzymes; the minisatellites are separated by gel electrophoresis; the pattern is determined by labelling the material with radioactive phosphorus-32 isotope and then either by using an X-ray film or by staining the sample with a fluorescent dye;
6. a) nitrogenous bases are held together by hydrogen bonds;
b) the information is coded by the sequence of nucleotides; each sequence of three nucleotides represents one amino acid (triplet code), which allows for up to 64 permutations (codons); the codons are translated into 20 naturally occurring amino acids; the complete sequence of nucleotides in the human DNA is known as the human genome;
7. possible responses can include the following: discussion of information and knowledge is impossible without the concept of data; data are facts describing the world; information is a snapshot of data; knowledge is a personal model of the world; information can be stored on any media while knowledge can be stored only in the human brain; data are always correct while both information and knowledge can be incorrect;
8. a) AUG-CCC-AGU-GCG-GCU-AGG-CAC-CGU-...
b) Met-Pro-Ser-Ala-Ala-Arg-His-Arg-...
9. possible responses can include the following: to some extent, the information about an individual's DNA is similar to the individual's personal data (name, bank account number, etc.) and therefore must be protected by law; uncontrolled access to DNA data can lead to discrimination and facilitate crime; access to DNA is needed for research, medical and legal purposes; a balance between the rights of individuals and the rights of society must be established;
10. a genetically modified food is derived (produced) from a genetically modified organism;
(i) benefits: (a) crops: enhanced taste/quality/appearance, reduced maturation time, increase in nutrients and yield, improved resistance to disease, pests and herbicides; (b) animals: improved health and increased productivity; (c) environment: "friendly" bio-herbicides and bio-insecticides, conservation of soil/water/energy, improved waste management; (ii) concerns: allergic reactions; altered composition of diet and nutritional quality of food; changes in ecosystems (including the development of "superweeds" and "superbugs"); lack of reliable data on long-term effects;

B.9 Questions (page 639)

1. a) a coloured compound produced by metabolism
b) electron conjugation (alternating single and double bonds)
c) photons are absorbed by molecules, causing electron transitions from lower to higher energy levels; electron conjugation lowers the energies of such transitions therefore reduces the frequency and increases the wavelength of absorbed radiation; if a large system of conjugation is present, this energy corresponds to visible light, which is absorbed; when a part of the spectrum is absorbed, the complementary colour becomes apparent (becomes dominant in the visible spectrum);
d) act as antioxidants, protect cells from UV radiation, participate in photosynthesis and vision, have signalling functions (e.g., attract insects to plants); some are vitamins and coenzymes.
2. hemoglobin contains iron and carries oxygen from lungs to cells; myoglobin contains iron and stores oxygen in muscle cells; cytochromes contain copper, magnesium and zinc and catalyse redox reactions (electron transport); chlorophyll contains magnesium and participate in photosynthesis;
3. refer to pages 633 and 634
4. tetracene, as it has a larger system of delocalized electrons (greater number of conjugated bonds)
5. a) when red, orange and/or yellow colours are absorbed, the complementary colour (blue) is transmitted
b) low pH and low temperature



6. beta-carotene absorbs light in blue/green region, so the complementary colours (red and orange) are transmitted
7. a) no effect, as it lies outside the visible spectrum (in the UV region)
b) the visible colour will be red, as it is complementary to the blue-green colour absorbed at 530 nm
8. a) anthocyanins contain many polar groups (such as -OH), which can form hydrogen bonds with water molecules
b) structure A (left) is more likely to exist in acid solutions because one of the oxygen atoms in this structure is protonated (which can only happen when the concentration of H^+ is high)
9. a) two
b) silica (SiO_2) or alumina (Al_2O_3);
c) component A (as it moves slower than component B)
d) the ratio between the distance moved by the spot and the distance moved by the solvent front ($R_f = L/L_0$)

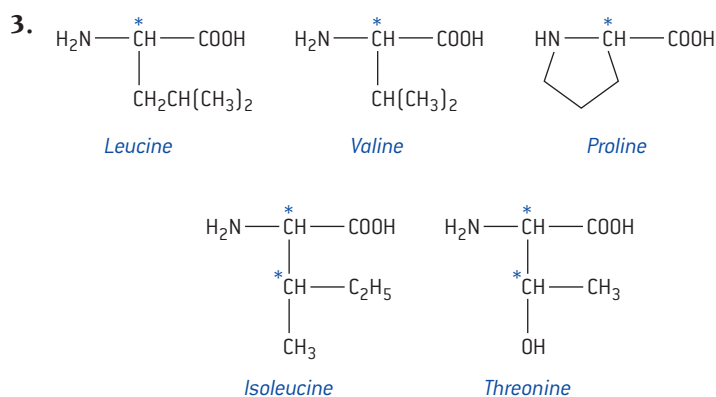


since the R_f of the banned substance is 0.25, its spot (shown in red) will travel approximately one-quarter of the distance between the starting point and the solvent front;

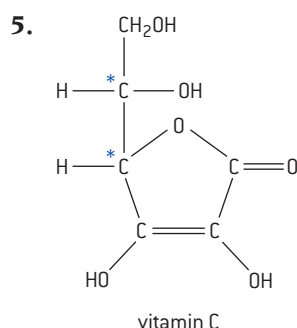
10. possible responses can include the following: each sense provides us with certain information about the world; using this information, individuals build their personal models of the world; information received from one sense can be confirmed and/or complemented by the information from other senses; information received from one sense can affect (alter) information received from other sense(s); contradictory information from different senses may cause confusion, alter perception and eventually lead to re-evaluation of individual's model of the world;

B.10 Questions (page 651)

1. a) they rotate the plane of polarization of a plane-polarized light by the same degree but in opposite directions
b) refer either to figure 2 on page 643 (wedge-dash notation), or figure 3 on the same page (Fischer projection), or figure 4 on page 644 (the CORN rule)
2. refer to figure 4 on page 644

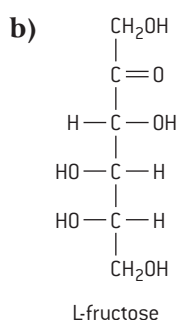
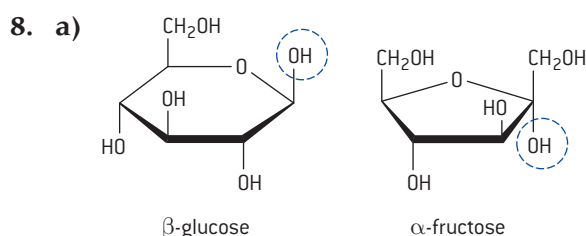


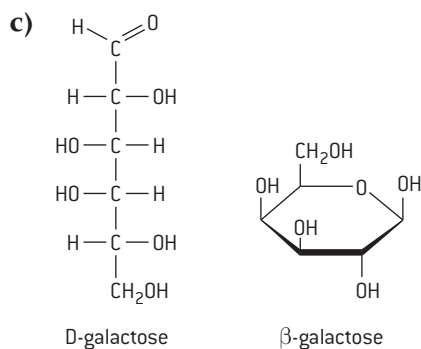
4. a) possible responses can include the discussion of how mutations, climate changes, environmental catastrophes, etc. may affect natural selection in small and large populations
- b) possible responses can include the following: such organism will have few or no natural enemies (as it will probably be toxic potential predators and its nutritional value will be lower than that of “normal” organisms); it might excrete toxic metabolites that will affect other organisms in the local ecosystem; at the same time, metabolites of “normal” organisms might be toxic to this artificial organism; depending on the structure of the local ecosystem and its own metabolism, such artificial organism might either multiply and spread uncontrollably, or develop a stable population, or become extinct in a short time; the exact outcome of the experiment is impossible to predict due to complexity of biological systems;



vitamin C contains two chiral carbon atoms; the other two compounds (2-BHA and BHT) do not contain any chiral carbon atoms;

6. enzymes are chiral biopolymers and therefore their active sites are also chiral; if one stereoisomer fits into an active site, another stereoisomer might not fit there and thus will not be metabolised (or will be metabolised slower, possibly by other enzymes, where it might fit into a different active site);
7. they differ by the orientation of the hydroxyl (–OH) group at the C-1 atom





9. a) both starch and cellulose are polymers of glucose; both contain glycosidic linkages. Starch is a polymer of α-glucose and consists of two components, amylose (straight-chain, contains only α-1,6-linkages) and amylopectin (branched, contains both α-1,6- and α-1,4-linkages); cellulose is a straight-chain polymer of β-glucose that contains only β-1,4-linkages;
- b) humans do not have the enzyme cellulase (or any other enzymes that can catalyse the hydrolysis of β-1,4-linkages in polysaccharides)
10. a) a plant material (mostly cellulose) that is mainly indigestible (not hydrolyzed by human enzymes)
- b) dietary fibre provides bulk to the diet, reduces appetite (and thus prevents obesity), accelerates the passage of food through the digestive system (prevents constipation), regulates blood sugar (and thus reduces the risk of diabetes), reduces risk of hemorrhoids, Crohn's disease, bowel cancer, and IBS;
11. a) saturated fats only: any acids with even number of carbon atoms (typically from C4 to C16), for example, lauric acid, palmitic acid, and stearic acid (refer to table 1 on page 566 for other names and structural formulae)
- b) *cis*-fats only: oleic acid, linoleic acid, and linolenic acid (refer to table 1 on page 566 for other names and structural formulae)
- c) *trans*-fats only: for example, elaidic acid and vaccenic acid (refer to table 1 on page 648 for structural formulae)
12. a) a transition metal catalyst (Ni, Cu, Pd, Pt), high temperature, and high pressure;
- b) *trans*-fats have *trans*-configuration of the carbon-carbon double bond(s); they are not easily digested, tend to accumulate in body tissues, and increase LDL cholesterol levels;
13. a) rhodopsin
- b) rhodopsin contains a residue of *cis*-retinal bound to the protein opsin; when rhodopsin absorbs a photon of visible light, the residue of *cis*-retinal isomerizes into *trans*-retinal; this isomerization triggers a cell response that sends an electrical signal to the nervous system, therefore, rhodopsin initiates a process that transforms light energy into electrical energy.

Option C - Energy

C.1 Questions (page 657)

- F
 - F
 - T
 - F
 - T
- 23400 kJ dm⁻³
 - 29.7 kJ g⁻¹
 - $\text{C}_2\text{H}_5\text{OH}(\text{l}) + 3\text{O}_2(\text{g}) \rightarrow 2\text{CO}_2(\text{g}) + 3\text{H}_2\text{O}(\text{l})$; 2 mol carbon dioxide per mol ethanol
 - growing the crops to produce the ethanol absorbs carbon dioxide.

C.2 Questions (page 664)

- $\text{C}_{12}\text{H}_{26} \rightarrow 2\text{C}_2\text{H}_4 + \text{C}_8\text{H}_{18}$
 - $\text{C}(\text{s}) + \text{H}_2\text{O}(\text{g}) \rightarrow \text{H}_2(\text{g}) + \text{CO}(\text{g})$
 - $\text{CO}(\text{g}) + 3\text{H}_2(\text{g}) \rightarrow \text{CH}_4(\text{g}) + \text{H}_2\text{O}(\text{l})$
 - $\text{C}_7\text{H}_{16} \rightarrow \text{C}_7\text{H}_8 + 4\text{H}_2$
 - $n\text{CO} + (2n + 1)\text{H}_2 \rightarrow \text{C}_n\text{H}(2n + 2) + n\text{H}_2\text{O}$; $7\text{CO}(\text{g}) + 15\text{H}_2(\text{g}) \rightarrow \text{C}_7\text{H}_{16}(\text{l}) + 7\text{H}_2\text{O}(\text{l})$
- 1.91 g
 - 2.75 g
 - 3.08 g
- ethanol: 30 kJ/g; methane: 56 kJ/g; high octane petrol (2,2,4-trimethylpentane): 48 kJ/g;
- ethanol produces the lowest CO₂ per gram fuel, but also has the lowest specific energy of the three; methane has a high specific energy, but due to it being a gas, it is difficult to compress to a usable form; 2,2,4-trimethylpentane is the most usable energy source in its form, but also produces the most carbon dioxide per gram of fuel used; the best green fuels should produce low CO₂, yet still yield high energy densities; biofuels may be an alternative as they consume carbon dioxide in the production of the fuel, thus no net increase in CO₂ levels as a result of their being burned;

C.3 Quick questions

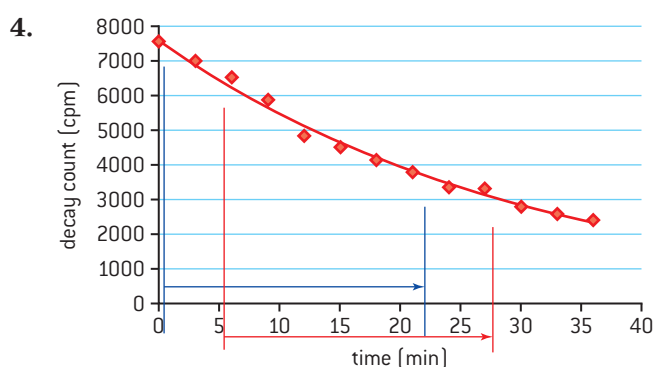
Page 670

- ${}^{131}_{53}\text{I} \rightarrow {}^{131}_{54}\text{Xe} + {}^0_{-1}\text{e}$ beta; decay;
 - ${}^{118}_{54}\text{Xe} + {}^0_{-1}\text{e} \rightarrow {}^{118}_{53}\text{I}$ beta; capture;
 - ${}^{226}_{88}\text{Ra} \rightarrow {}^{222}_{86}\text{Rn} + {}^4_2\text{He}$ alpha; decay;
 - ${}^{212}_{83}\text{Bi} \rightarrow {}^4_2\text{He} + {}^{208}_{81}\text{Tl}$ alpha; decay;
- ${}^1_1\text{H} + {}^3_1\text{H} \rightarrow {}^4_2\text{He}$
 - ${}^{235}_{92}\text{U} + {}^1_0\text{n} \rightarrow {}^{139}_{56}\text{Ba} + {}^{94}_{36}\text{Kr} + 3 {}^1_0\text{n}$
 - ${}^6_3\text{Li} + {}^1_0\text{n} \rightarrow {}^0_{-1}\text{e} + {}^4_2\text{He} + {}^3_2\text{He}$
- ${}^{24}_{11}\text{Na} \rightarrow {}^{24}_{12}\text{Mg} + {}^0_{-1}\text{e}$
 - ${}^{17}_9\text{F} \rightarrow {}^0_{+1}\text{B} + {}^{17}_8\text{O}$
 - ${}^{241}_{95}\text{Ra} \rightarrow {}^{237}_{93}\text{Np} + {}^4_2\text{He}$

4. a) nuclear binding energy peaks around the element iron; elements with atomic numbers less than iron fuse nuclei to increase binding energy, whereas elements with atomic numbers much greater than iron will undergo fission to form the lighter more stable nuclei closer to the iron peak;
- b) the fission of hydrogen nuclei to helium shows a much larger mass defect (binding energy) than does the fission of uranium to lighter nuclei; this large mass defect is converted into energy ($E = mc^2$);

Page 671

1. 1250 cpm
2. 5.0 g
3. ${}^{60}_{27}\text{Co} \rightarrow {}^{60}_{28}\text{Ni} + {}^0_{-1}\text{e}$; 0.5 mg of daughter product obtained



From chart, $\frac{1}{2}$ life approximately 20 years.

Questions (page 673)

1. a proton or a neutron
2. emission and absorption spectra observed from the sun
3. the half-life ($t_{1/2}$) refers to the time it takes for one half of the number of atoms in a sample to decay
4. 10 ± 1 hours
5. a) ${}^{98}_{42}\text{Mo} + {}^1_0\text{n} \rightarrow {}^0_{-1}\text{e} + {}^{99m}_{43}\text{Tc}$
 - b) $\frac{1}{2}$ of the ${}^{99m}_{43}\text{Tc}$ will undergo transmutation to ${}^{99}_{43}\text{Tc}$ in 6 hours
 - c) 16.0×10^{-9} g or 1.6×10^{-8} g
6. a) $a = 239$; $b = 93$; $c = 239$; $d = 94$;
 - b) $X = \text{Np}$; $Y = \text{Pu}$;
7. light nuclei for fusion; heavy nuclei for fission; more massive nucleus produced in fusion / joined together; two lighter nuclei produced in fission / splits apart;
8. a) mass defect: the mass of a nucleus is less than the masses of its constituent particles; the difference is the mass defect;
 - b) nuclear binding energy is the energy required to separate a nucleus into its constituent parts, namely protons and neutrons
 - c) binding energy of the nucleus divided by the sum of its nucleons (protons + neutrons)
9. a) 0.0184 amu mass defect; 17MeV;
 - b) more atoms of hydrogen in 1g of hydrogen than in 1 g of U-235; obtaining U-235 is energy intensive; hydrogen is plentiful (can be obtained from electrolysis of water);



C.4 Questions (page 678)

- $6\text{CO}_2 + 6\text{H}_2\text{O} \rightarrow \text{C}_6\text{H}_{12}\text{O}_6 + 6\text{O}_2$
- ethanol produced from fermentation by plants which absorb CO_2 in growing
- in transesterification, a methyl ester is typically produced to be used as the biodiesel; a vegetable oil is heated with methanol to produce the methyl ester, or heated with ethanol to produce the ethyl ester; in both cases they need to be heated with a catalyst, such as sodium or potassium hydroxide; vegetable oil is a triglyceride, so three of the methyl or ethyl esters are produced as well as glycerol;
- vegetable oils can produce similar energy when burned but because they are so viscous, they are unable to flow easily and can clog fuel injectors; high viscosity implies large intermolecular forces; this means these oils do not readily vaporize and often undergo incomplete combustion which further damages engines; this problem is overcome by converting them to a more viscous form with fewer IMF; a triglyceride is converted to an ester and glycerol; this is a transesterification process;
- an extended system of alternating single and multiple bonds
- vitamin A as it has the highest degree of conjugation
- $\text{C}_6\text{H}_{12}\text{O}_6 \rightarrow 2\text{C}_2\text{H}_5\text{OH} + 2\text{CO}_2$
- $\text{RCOOR}' + \text{R}''\text{OH} \rightarrow \text{RCOOR}'' + \text{R}'\text{OH}$
- 3 molecules of ester and glycerol per molecule of triglyceride
- see chart on page 677

C.5 Questions (page 686)

- while water vapour quantities in the atmosphere haven't varied a lot, the other gases, particularly CO_2 have increased significantly since the beginning of the industrial revolution
- water, carbon dioxide, and methane all of which occur naturally; CO_2 , NO_x and methane also have anthropogenic sources such as industry and agriculture;
- stretching/bending; causing a change in polarity/dipole moment;
- the reflected radiation interacts with the bonds of these molecules in the atmosphere trapping the energy in the earth's atmosphere as opposed to allowing it to re-radiate to space;
- particulate matter from industrial processes can reflect light causing global dimming; without this effect for the three days of air traffic and industry closure the effect of global dimming was lessened, allowing more radiation to reach the surface and increase warming;
- once gaseous carbon dioxide dissolves, eg: $\text{CO}_{2(\text{g})} \rightarrow \text{CO}_{2(\text{aq})}$, the equilibrium reaction to carbonic acid $\text{H}_2\text{CO}_{3(\text{aq})}$ is rapid; the reaction in water can change the pH;

$$\text{H}_2\text{CO}_3 + \text{H}_2\text{O} \leftrightarrow \text{H}_3\text{O}^+ + \text{HCO}_3^-; \quad \text{HCO}_3^- + \text{H}_2\text{O} \leftrightarrow \text{H}_3\text{O}^+ + \text{CO}_3^{2-}$$
gaseous CO_2 is only very slightly soluble in water, so the pH change has only been slight;
 - equilibrium shifts to the left, increasing pH slightly
 - all gases have higher KE at higher temperatures and are therefore less soluble
- smoke, dust particles, and clouds can reflect sunlight back to space, causing global dimming and the earth's surface to cool; some effects are acid rain due to reaction of gases with water/decrease rate of evaporation/ less monsoonal rain/more drought/health concerns from particulate matter, eg asthma;

C.6 Questions (page 701)

- answer needs to be rationalized in terms of energy density/specific energy; quantity available; ease of production/transport; renewability;
- the nature of material; the further apart the oxidising and reducing materials are on their respective standard electrode potentials, the more voltage per cell is available;



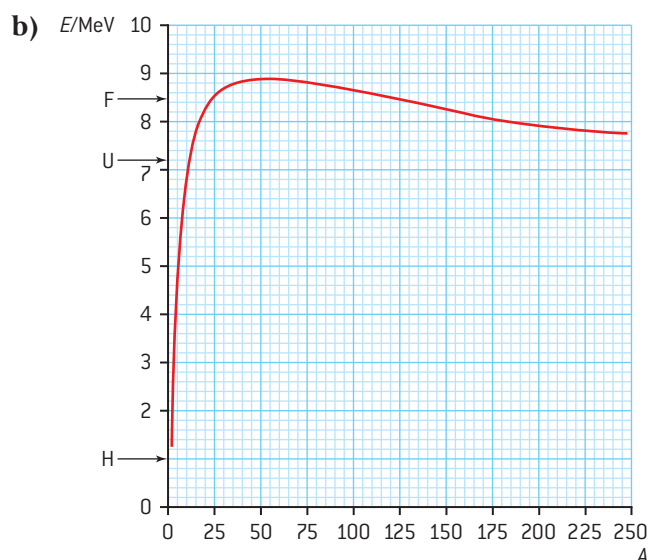
- b) the quantity of material and its specific energy density give a measure of the work which can be done; the total number of electrons moving as well as the push behind them gives a measure of how much work can be done;
- c) large thick plates increase the quantity of material (work); placing these in series allows for more push per electron (voltage);
- 3. a battery's internal resistance depends on ion mobility, electrolyte conductivity, and electrode surface area; all reactions occur faster at higher temperatures; colder temperatures will cause rates to slow down, lessen ion mobility, and increase a battery's internal resistance;
- 4. lithium ion batteries have higher charge densities, contain no heavy metals, can be recharged many times; Ni-Cad batteries have lower internal resistance and can be fully discharged for high drain applications; they operate better at higher temperatures and have a fast recharge time;
- 5. a) gain of electrons = reduction and occurs at the cathode; charging reaction;
 b) $\text{LiCoO}_{2(s)} \rightarrow \text{Li}^+ + \text{e}^- + \text{CoO}_{2(s)}$
 c) lithium is highly reactive and battery could explode if exposed to air or moisture;
- 6. a polymer which allows the small H^+ ions to diffuse through, but does not allow electrons or molecules to pass through; in microbial fuel cells anaerobic oxidation produces H^+ ions and electrons; the electrons can be harnessed at an anode and the H^+ ions permitted to diffuse through a proton exchange membrane (PEM) where they reduce oxygen;
- 7. a) 96%
 b) ethanol and methanol are both liquids at room temperature, so having a higher energy per unit volume is an advantage when transport of the fuel is concerned; ethanol produced in microbial fuel cells; biological sources of ethanol; easier production and availability;
- 8. 0.14V; lower concentration (0.1M) being oxidized;
- 9. a) Al electrode: anode and oxidized, Zn electrode: cathode and reduced; appropriate diagram showing electron flow from Al electrode to Zn; positive ions moving through solution to cathode side (Zn), negative ions toward anode (Al);
 b) 0.91V
- 10. microbial fuel cells can be very compact and could possibly be developed to produce electricity from human waste; DMFC have high energy densities; hydrogen fuel cells are clean source of energy;

C.7 Questions (page 708)

- 1. a) nuclear energy benefitted from the race to develop nuclear weapons
 b) $\Delta m = 234.99333 - 135.90722 - 89.907738 - [9 \times 1.00867] = 0.100342 \text{ (u)}$; $0.100342 \times 1.661 \times 10^{-27} \text{ kg} = 1.67 \times 10^{-28} \text{ kg}$; (use of $E = mc^2$) energy = $1.67 \times 10^{-28} \times (3 \times 10^8)^2 = 1.50 \times 10^{-11} \text{ J}$
 c) $\lambda \left(= \frac{\ln 2}{t_{1/2}} = \frac{\ln 2}{28.8} \right) = 0.0241$

$$t \left(= -\frac{1}{\lambda} \ln \frac{N}{N_0} = -\frac{\ln 0.1}{0.0241} \right) = 95.7 \text{ years}$$

 d) conversion to UF_6 ; different isotopes have different rates of diffusion; gases diffuse at rate proportional to $(M_r)^{-\frac{1}{2}}$; diffusion produced by ultracentrifuges;
- 2. D
- 3. b
- 4. a) (i) a proton or a neutron
 (ii) the difference between the mass of the nucleus and the sum of the masses of its individual nucleons or the energy required to separate a nucleus into its component nucleons;



(i) F: between 8 and 9

(ii) H: between 1 and 2

(iii) U: between 7 and 8

c) general overall shape; max at F = 56, end point U;

d) mass of nucleons = $(2 \times 1.00728) + 1.00867 = 3.02323 \text{ u}$

mass difference = $0.0072 \text{ u} = 6.7 \text{ MeV}$

binding energy per nucleon = $\frac{6.7}{3} = 2.2 \text{ MeV}$

e) (i) fusion

(ii) from the position on the graph, the energy required to assemble two nuclei of ${}^2_1\text{H}$ is greater than that to assemble one nucleus of ${}^3_2\text{He}$; hence, if two nuclei of ${}^2_1\text{H}$ combine to form one nucleus of ${}^3_2\text{He}$ energy must be released;

5. a) (i) fuel enrichment means that the amount of uranium-235 present in the fuel is increased; this means that more U-235 available for fission; therefore the reaction can be sustained;

(ii) enriched fuel can be used in the manufacture of nuclear weapons; so possibly threatening World peace;

(iii) Graham's law states that the rate of effusion of two gases is inversely proportional to the square root of their molar masses at the same temperature and pressure; $\text{KE} ({}^{235}\text{F}_6) = \text{KE} ({}^{238}\text{F}_6)$;
 $\frac{1}{2}mv^2 ({}^{235}\text{F}_6) = \frac{1}{2}mv^2 ({}^{238}\text{F}_6)$;

$$\frac{v \text{ U235 isotope}}{v \text{ U238 isotope}} = \sqrt{\frac{MM \text{ U238 isotope}}{MM \text{ U235 isotope}}}$$

b) (i) uranium hexafluoride has an octahedral shape, is non-polar, and very volatile (high vapour pressure) due to the very weak intermolecular forces when compared to UO_2

(ii) solid UF_6 is vaporised and forced through a porous membrane at an increased pressure; because the U-235 isotope is lighter, it moves through the membrane more easily; in the gas centrifuge process the gaseous UF_6 is introduced in a flowing current form opposite to that at which a centrifuge separator is spinning; the heavier U-238 tends to remain closer to the wall due to the centripetal force and the somewhat enriched U-235 is then withdrawn; this only increases the concentration by minimal amounts so many stages are necessary;



6. x = distance travelled by NH_3 ; $1-x$ = distance travelled by HCl

$$\frac{v_{\text{NH}_3}}{v_{\text{HCl}}} = \sqrt{\frac{MM_{\text{HCl}}}{MM_{\text{NH}_3}}}$$

$$\frac{x}{1-x} = \sqrt{\frac{36.5}{17}}$$

$x = 65$ cm mark

7. see figure 6 on page 708; $\cdot\text{OH}$ /hydroxyl has an unpaired electron on O and no charge; the term free-radical refers to a species that is formed when a molecule undergoes homolytic fission: the two electrons of a covalent bond are split evenly between two atoms resulting in two free-radicals that each have a single electron; there are three stages involved in such free-radical substitution reactions: initiation, propagation, and termination {see Topic 10.2, page 251 for description}; radioactivity acts serves to raise the energy sufficient enough to cause the initiation step;

C.8 Questions (page 716)

- dye sensitised cells can use light of lower energy/lower frequency/longer wavelength than silicon cells; nanoparticles provide a large surface area; light energy excites dye molecules; dye molecules inject electrons into TiO_2 layer; dye molecules that have lost electrons oxidize/convert I^- (in electrolyte) to I_2/I_3^- ; electrons flow through external circuit back to counter electrode; electrons turn/reduce I_2/I_3^- ions to I^- (at the counter electrode);
- 1,3-hexadiene absorbs the longer wavelength as 1,5-hexadiene does not undergo conjugation but 1,3-hexadiene does
- B^- has the higher conjugation as organic indicators are in the equilibrium of $\text{RCOOH} \leftrightarrow \text{H}^+ + \text{RCOO}^-$;

RCOO^- can undergo more conjugation than RCOOH ; the yellow form absorbs violet light of around 410nm, while the blue form absorbs orange light of around 620 nm; the longer the wavelength absorbed, the higher the conjugation; B^- is blue and absorbs longer wavelengths of light, hence has a higher degree of conjugation.



Option D – Medicinal chemistry

D.1 Questions (page 724)

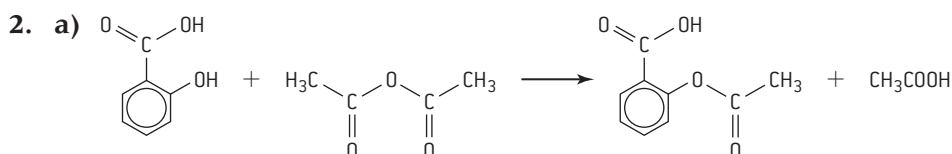
1.
 - a) refer to page 719 and the side box on page 720
 - b) by a double-blind test, in which laboratory animals or human volunteers are divided into two groups; one group receives the drug, another group receives a placebo; neither the researchers nor the volunteers know who gets the drug and who gets the placebo; the therapeutic effects in the two groups are compared; the difference is attributed to the drug action;
2.
 - a) alters mood, emotions, or incoming sensory sensations
 - b)
 - (i) the range over which a drug can be safely administered (refer to page 720 for more information)
 - (ii) person needs ever increasing dose of a drug to gain the original effect
3. modelling of the three-dimensional shape of the drug molecule and/or the target molecule (or drug receptor); modelling the interaction of the drug with the target molecule; prediction of how changes in the drug structure will affect its interactions with the target molecule;
4.
 - a) C
 - b) A and/or B
 - c) A
5.
 - a) advantages: convenient (easily taken); no specialist equipment needed; disadvantages: stomach acid might deactivate the drug; slow effect; low bioavailability (only a fraction of the drug can be absorbed); can harm digestive system (cause stomach bleeding) or cause unpleasant effect (vomiting); requires a conscious patient;
 - b) inhalation; injection (parenteral, intravenous, intramuscular, subcutaneous); rectal; transdermal; other methods (vaginal, nasal, ophthalmic, etc.) are also possible;
6.
 - a) intravenous, because the drug is quickly transported by the blood to various parts of body
 - b) intramuscular and subcutaneous; other methods (such as intracerebral) are also possible;
 - c) inhalation
7.
 - a) drugs can affect the physiological state of the body, alter mood and emotions, or change the perception of sensory information
 - b) non-beneficial or unintended effect of the drug on the human body
 - c) perceived or actual improvement in a medical condition as a result of a simulated medical treatment; it is commonly observed when a patient is given a biologically inert substance (placebo) that he/she believes to be a medical drug; such deception may stimulate the body's natural healing processes; the possibility of a placebo effect must be taken into account when new drugs are tested on humans; placebo must be used as a control in double-blind trials (refer to answer 1 (b) for full explanation);
8. main stages: identification of a lead compound (by drug design/discovery/screening); preparation of the drug analogues; characterization of the drug (*in vitro* testing); preclinical trials (on animals/bacteria/cell cultures); clinical trials (on humans), including phase I (on healthy volunteers) and phases II/III (on patients); post-clinical studies (phase IV trials);
9. enzymes and cellular receptors are mostly proteins that have certain chemical structures and three-dimensional shapes; the structures of drugs are complementary to the structures of active (or allosteric) sites of enzymes or receptors; drugs bind to these sites as described by the "lock and key" and "induced fit" models (refer to pages 561 and 611); most drugs act as enzyme inhibitors (competitive or non-competitive — refer to pages 611 and 612); drugs that bind to receptors trigger cellular responses;



10. possible responses can include the following: the names of drugs are often informative (related to their structures, properties, origins, etc.), easy to remember and designed to attract attention; “good” names can influence the choices made by customers (patients and medical practitioners) and promote certain drugs and/or drug manufacturers; in some cases (such as placebo labelling), descriptive names should be avoided; some legislations require certain drugs to have neutral and/or non-descriptive names;
11. possible responses can include the following: individuals have rights to make choices about their own health and quality of life; some people believe that the freedom to use and abuse drugs (both medical and narcotic) is a fundamental human right; poor choices of individuals negatively affect the entire society (by increasing the cost of health, social and law enforcement services, reducing the productivity of workforce and therefore the taxes collected by the government, etc.); children must be protected by the society from all forms of drug abuse, including inadequate choices made by their parents (e.g., treating common cold with antibiotics, giving sedatives to crying babies, etc.); the availability of drugs can be regulated in many ways, from licensing and prescription to prohibition; drug-related regulations and traditions vary greatly around the world;

D.2 Questions (page 731)

1. a) prostaglandins are involved in the transmission of pain impulses to the brain; when the production of prostaglandins is suppressed, the pain impulses do not reach the brain;
- b) prevention of heart attacks and strokes, reduction of blood clotting, anti-inflammatory action

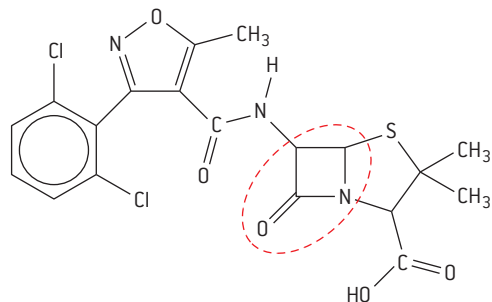


- b) condensation / nucleophilic substitution;
- c) ten tablets will contain $10 \times 500 \text{ mg} = 5000 \text{ mg} = 5 \text{ g}$ of acetylsalicylic acid ($\text{C}_9\text{H}_8\text{O}_4$)
 $M(\text{C}_9\text{H}_8\text{O}_4) = 9 \times 12.01 + 8 \times 1.01 + 4 \times 16.00 = 180.17 \text{ g mol}^{-1}$
 $n(\text{C}_9\text{H}_8\text{O}_4) = 5 \text{ g} / 180.17 \text{ g mol}^{-1} \approx 0.0277 \text{ mol}$
 If the yield is 60%, the amount of salicylic acid ($\text{C}_7\text{H}_6\text{O}_3$) is $0.0277 / 0.6 \approx 0.0462 \text{ mol}$
 $M(\text{C}_7\text{H}_6\text{O}_3) = 7 \times 12.01 + 6 \times 1.01 + 3 \times 16.00 = 138.13 \text{ g mol}^{-1}$
 $m(\text{C}_7\text{H}_6\text{O}_3) = 138.13 \text{ g mol}^{-1} \times 0.0462 \text{ mol} \approx 6.4 \text{ g}$
3. advantages: does not cause stomach ulceration/bleeding, produces fewer allergic reactions, does not cause Reye's syndrome; disadvantages: may cause blood disorders, may cause kidney, liver and brain damage; is not an anti-inflammatory drug;
4. increased risk of stomach bleeding
5. a) fluoxetine has an amino group ($-\text{NH}_2$) that can be converted into a salt by the reaction with hydrochloric acid (HCl) or any other strong acid; aspirin has a carboxyl group ($-\text{COOH}$) that can be converted into a salt by the reaction with sodium hydroxide (NaOH) or any other strong base;
- b) it increases the drug's solubility in water and therefore facilitates the drug's distribution in the body
6. a) he left a Petri dish with bacteria open and later noticed that the penicillin mould contaminated the dish and inhibited bacterial growth
- b) they overcame problems associated with isolating/concentrating penicillin, showed that penicillin was harmless and effective on mice, developed techniques to purify penicillin, were the first to use penicillin on a person, grew strains of penicillin in bulk using corn-steep liquor;
- c) penicillin interferes with the enzymes that bacteria need to make cross-links in cell walls; due to osmotic pressure, water enters bacterial cells with weakened walls, causing the bacteria to burst and die;



d) amido group (amide)

e)



all bond angles in the β -lactam ring are approximately 90° (instead of 109 and 120°), which causes ring strain; the amido group in the strained ring is very reactive; the strained ring breaks (opens) easily and reacts with (irreversibly bonds to) bacterial enzymes;

f) the resistance is caused by overprescription/overuse of penicillins, non-compliance of patients (as some patients do not complete their course of antibacterials), and the use of antibiotics in animal feed (to stimulate growth and increase productivity of healthy animals); to overcome bacterial resistance, penicillins with modified side chains must be developed and/or cocktails of antibacterials must be used;

7. each course of antibacterials must be completed, otherwise, the most resistant bacteria may survive the treatment; when the course is terminated too early, these bacteria will multiply and pass their resistance to future generations;
8. possible responses can include the following: the formation of mould and its effects on bacterial cultures had been noticed before Fleming's discovery but dismissed by other researchers; some researchers are too focussed on a particular problem and therefore can easily overlook or reject any data not directly related to this problem; personal interests and beliefs can significantly affect our perception, increasing the apparent importance of some data and making other data seemingly irrelevant or unimportant; the lack of open-mindedness can lead to selective approach to experimental data and ultimately to wrong conclusions (e.g., a wrong theory can be "confirmed" by an unrepresentative subset of experimental data);

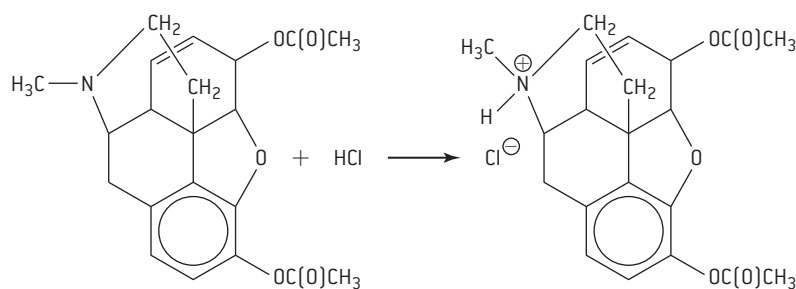
D.3 Questions (page 736)

1. a) amino group, ether group, unsaturation (double $C=C$ bond), aromatic (benzene) ring;
b) (phenolic) hydroxyl group ($-OH$)
c) condensation / esterification / acylation / nucleophilic substitution;
2. a) mild analgesics: suppress the production of prostaglandins, intercepting the pain stimulus at the source; strong analgesics: bind to opioid receptors in the brain/central nervous system;
b) advantages: strong analgesics (can relieve acute pain), wide therapeutic window, relieve anxiety, induce relaxation, improve the quality of life; can be injected intravenously for fast effect; disadvantages: euphoria (loss of self-control, dangerous behaviour), addiction and withdrawal symptoms, tolerance (increased risk of overdose upon prolonged use), kidney failure, risks associated with intravenous drug administration;
c) heroin is less polar than morphine (due to the replacement of polar OH groups with less polar ester groups), so it is more soluble in non-polar environment of the CNS and can easily cross the blood-brain barrier
3. a) ester / ethanoate
b) possible reagents: ethanoic (acetic) anhydride, ethanoyl (acetyl) chloride, ethanoic (acetic) acid; reaction type: condensation / esterification / acylation / nucleophilic substitution;



4. a) (tertiary) amino group

b)



c) increased (if the drug is administered orally); in the case of intravenous injection, the bioavailability will not change, as it is always assumed to be 100%;

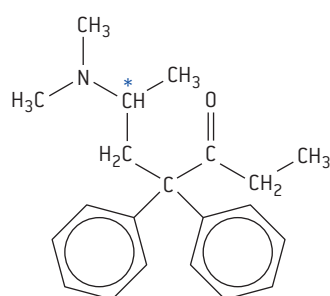
5. a) morphine (as it contains the greatest number of polar functional groups)

b) it will form multiple hydrogen bonds with water due to the presence of two polar hydroxyl groups and one polar tertiary amino group;

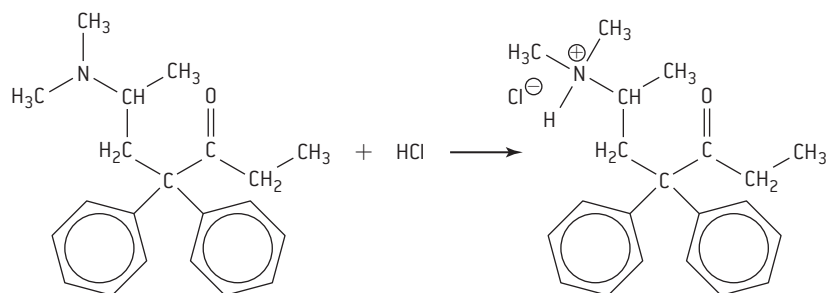
c) diamorphine (as it contains the smallest number of polar functional groups)

6. a) (tertiary) amino group, carbonyl (ketone) group, aromatic (phenyl, or benzene) rings;

b)



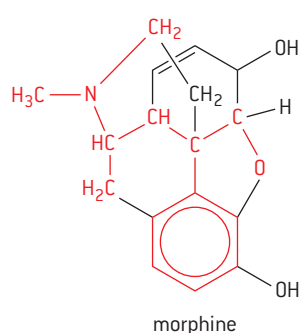
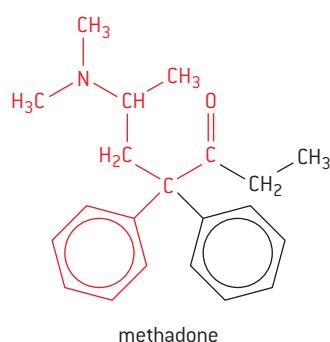
c)



d) methadone hydrochloride will be more soluble in water and will have higher bioavailability if administered orally; bioavailability of any drug injected intravenously is always 100%;

e) strong analgesic, as its mechanism of action is similar to that of opiates

f) tertiary amino group and a phenyl ring (in both compounds), carbonyl group in methadone and ester group in morphine; structurally similar fragments in the molecules of methadone and morphine are shown below in red;





7. possible responses can include the following: no, as nations/ethnic groups have a right to live the way they want; yes, as other nations/ethnic groups have a right to protect themselves from negative consequences of drug abuse; illegal drug production and trafficking is a global problem that can be resolved only at the international level;

D.4 Questions (page 744)

1. $c(\text{H}^+) = 10^{-\text{pH}} = 10^{-1.5} \approx 0.03 \text{ mol dm}^{-3}$ (the result is rounded to one significant figure, as the mantissa has one digit)

HCl is a strong acid, so $c(\text{HCl}) = c(\text{H}^+) = 0.03 \text{ mol dm}^{-3}$

let $V(\text{sample}) = 1.00 \text{ dm}^3$, then $m(\text{sample}) = 1.03 \text{ kg} = 1030 \text{ g}$ and $n(\text{HCl}) = 0.03 \text{ mol}$

$M(\text{HCl}) = 1.01 + 35.45 = 36.46 \text{ g mol}^{-1}$

$m(\text{HCl}) = 36.46 \text{ g mol}^{-1} \times 0.03 \text{ mol} \approx 1 \text{ g}$

$\omega(\text{HCl}) = (1 \text{ g} / 1030 \text{ g}) \times 100\% \approx 0.1\%$

2. a) $\text{Al}(\text{OH})_3(\text{s}) + 3\text{HCl}(\text{aq}) \rightarrow \text{AlCl}_3(\text{aq}) + 3\text{H}_2\text{O}(\text{l})$

$\text{MgCO}_3(\text{s}) + 2\text{HCl}(\text{aq}) \rightarrow \text{MgCl}_2(\text{aq}) + \text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{l})$

- b) $n(\text{Al}(\text{OH})_3) = 0.160 \text{ g} / 77.95 \text{ g mol}^{-1} \approx 0.00205 \text{ mol}$

$n(\text{MgCO}_3) = 0.105 \text{ g} / 84.32 \text{ g mol}^{-1} \approx 0.00125 \text{ mol}$

according to equations in (a), $\text{Al}(\text{OH})_3$ will neutralize $3 \times 0.00205 = 0.00615 \text{ mol}$ of HCl while MgCO_3 will neutralize $2 \times 0.00125 = 0.00250 \text{ mol}$ of HCl, therefore $\text{Al}(\text{OH})_3$ will neutralize more acid than MgCO_3 ;

- c) produces a protective layer that floats on top of the stomach contents and prevents the gastric juice from rising into the esophagus (heartburn/reflux)

3. $\text{Mg}(\text{OH})_2(\text{s}) + 2\text{HCl}(\text{aq}) \rightarrow \text{MgCl}_2(\text{aq}) + 2\text{H}_2\text{O}(\text{l})$

$d(\text{sample}) = 1.15 \text{ kg dm}^{-3} = 1.15 \text{ g cm}^{-3}$

$m(\text{sample}) = 2.00 \text{ cm}^3 \times 1.15 \text{ g cm}^{-3} = 2.30 \text{ g}$

$V(\text{HCl solution}) = 15.8 \text{ cm}^3 = 0.0158 \text{ dm}^3$

$n(\text{HCl}) = 0.0158 \text{ dm}^3 \times 0.400 \text{ mol dm}^{-3} = 0.00632 \text{ mol}$

according to the neutralization equation, $n(\text{Mg}(\text{OH})_2) = 0.00632 \text{ mol} / 2 = 0.00316 \text{ mol}$

$M(\text{Mg}(\text{OH})_2) = 24.31 + (16.00 + 1.01) \times 2 = 58.33 \text{ g mol}^{-1}$

$m(\text{Mg}(\text{OH})_2) = 0.00315 \text{ mol} \times 58.33 \text{ g mol}^{-1} \approx 0.184 \text{ g}$

$\omega(\text{Mg}(\text{OH})_2) = (0.184 \text{ g} / 2.30 \text{ g}) \times 100\% = 8.00\%$

4. a) hydroxides of alkali metals are strong bases, which are harmful to the body (they can damage cellular tissues, denature proteins, etc.)

- b) alginates: refer to answer 2 (c); dimethicone: an anti-foaming agent that prevents flatulence/bloating;

5. possible responses can include the following: antacids act quickly but provide only a short-term relief as they do not target the cause of the problem (overproduction of the stomach acid); H_2 -receptor antagonists control the acid secretion at the cellular level but also require frequent administration; the proton pump inhibitors suppress the acid secretion for prolonged periods of time but are more likely to cause side effects, especially in the case of an overdose;

6. a) ethanoic acid is the conjugate acid; acetate ions (from sodium acetate) are the conjugate base; according to table 1 on page 741, $\text{p}K_a(\text{CH}_3\text{COOH}) = 4.76$

$V(\text{buffer solution}) = 500 \text{ cm}^3 = 0.500 \text{ dm}^3$

$n(\text{CH}_3\text{COONa}) = 16.4 \text{ g} / 82.04 \text{ g mol}^{-1} = 0.200 \text{ mol}$

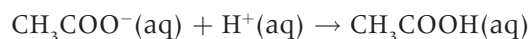
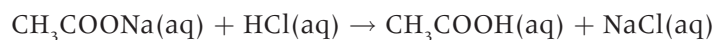


$$c(\text{CH}_3\text{COONa}) = 0.200 \text{ mol} / 0.500 \text{ dm}^3 = 0.400 \text{ mol dm}^{-3}$$

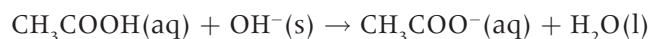
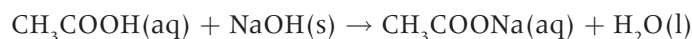
$$\text{pH} = 4.76 + \log \frac{[\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} = 4.76 + \log \frac{0.400}{0.100} \approx 5.36$$

b) From 3.76 to 5.76 (i.e., $\text{p}K_a \pm 1$)

c) HCl will react with the conjugate base:



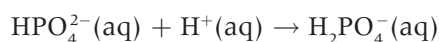
sodium hydroxide will react with the conjugate acid:



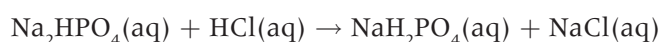
7. a) the pH of the solution (6.8) is within $\text{p}K_{a2} \pm 1$ range; according to table 1 on page 741, the buffer system consists of H_2PO_4^- (conjugate acid) and HPO_4^{2-} (conjugate base);

b) according to the Henderson–Hasselbalch equation, $6.80 = 7.20 + \log \frac{[\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]}$, so $\log \frac{[\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]} = -0.4$ and therefore $\frac{[\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]} = 10^{-0.4} \approx 0.4$; the amounts of ions are proportional to their concentrations, so the mole ratio of HPO_4^{2-} to H_2PO_4^- is 2 : 5;

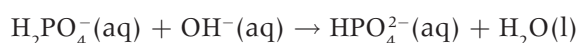
c) reaction with a strong acid:



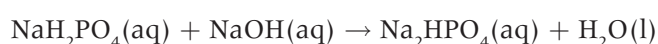
the buffer was prepared from phosphoric acid and sodium hydroxide, so HPO_4^{2-} corresponds to Na_2HPO_4 and H_2PO_4^- corresponds to NaH_2PO_4 ; assuming that the strong acid is HCl, we can deduce the molecular equation:



reaction with a strong base:



assuming that the strong base is NaOH, the molecular equation will be:



d) the ratio will remain approximately the same, as the pH of an acid-base buffer is independent of dilution

8. in our buffer solution, ammonium (NH_4^+) is the conjugate acid and ammonia (NH_3) is the conjugate base; according to the Henderson–Hasselbalch equation,

$$8.8 = 9.25 + \log \frac{0.200}{[\text{NH}_4^+]}, \text{ so } \log \frac{0.200}{[\text{NH}_4^+]} = -0.45 \text{ and } [\text{NH}_4^+] = \frac{0.200}{10^{-0.45}} \approx 0.56 \text{ mol dm}^{-3}$$

ammonium ions are produced by the dissociation of ammonium chloride:



according to this equation, the concentration of ammonium chloride is the same as the concentration of ammonium ions, 0.56 mol dm^{-3} , therefore:

$$n(\text{NH}_4\text{Cl}) = 0.100 \text{ dm}^3 \times 0.56 \text{ mol dm}^{-3} = 0.056 \text{ mol}$$

$$m(\text{NH}_4\text{Cl}) = 0.056 \text{ mol} \times 53.50 \text{ g mol}^{-1} \approx 3.0 \text{ g}$$

9. $300 \text{ cm}^3 = 0.3 \text{ dm}^3$

let $V(\text{Na}_2\text{CO}_3 \text{ solution}) = x \text{ dm}^3$, then $V(\text{NaHCO}_3 \text{ solution}) = (0.3 - x) \text{ dm}^3$

$$n(\text{Na}_2\text{CO}_3) = 0.100x \text{ mol}, n(\text{NaHCO}_3) = 0.100(0.3 - x) \text{ mol}$$

$$c(\text{Na}_2\text{CO}_3) = 0.100x/0.3 \text{ mol dm}^{-3}; c(\text{NaHCO}_3) = 0.100(0.3 - x)/0.3 \text{ mol dm}^{-3}$$



Na_2CO_3 is the conjugate base and NaHCO_3 is the conjugate acid; according to the Henderson–Hasselbalch equation:

$$10.0 = 10.3 + \log \frac{\frac{0.100x}{0.3}}{\frac{0.100(0.3-x)}{0.3}}$$

$$\frac{x}{0.3-x} = 10^{-0.3} \approx 0.5$$

$$x = 0.15 - 0.5x$$

$$1.5x = 0.15$$

$$x = 0.1 \text{ (dm}^3\text{)}$$

therefore, we need to mix together $0.1 \text{ dm}^3 = 100 \text{ cm}^3$ of the Na_2CO_3 solution and $(0.3 - 0.1) \text{ dm}^3 = 200 \text{ cm}^3$ of the NaHCO_3 solution;

$$10. V(\text{HCl solution}) = 50.0 \text{ cm}^3 = 0.0500 \text{ dm}^3$$

$$n(\text{HCl}) = 0.0500 \text{ dm}^3 \times 10.0 \text{ mmol dm}^{-3} = 0.500 \text{ mmol} = 5.00 \times 10^{-4} \text{ mol}$$

$$n(\text{Na}_2\text{CO}_3) = 0.100 \text{ dm}^3 \times 0.100 \text{ mol dm}^{-3} = 1.00 \times 10^{-2} \text{ mol}$$

$$n(\text{NaHCO}_3) = 0.200 \text{ dm}^3 \times 0.100 \text{ mol dm}^{-3} = 2.00 \times 10^{-2} \text{ mol}$$

the strong acid (HCl) will react with the conjugate base (Na_2CO_3) of the buffer system:

	Na_2CO_3 +	HCl →	NaHCO_3	+ NaCl
$n_{\text{init}}, \text{mol}$	1.00×10^{-2}	5.00×10^{-4}	2.00×10^{-2}	—
$\Delta n, \text{mol}$	-5.00×10^{-4}	-5.00×10^{-4}	$+5.00 \times 10^{-4}$	$+5.00 \times 10^{-4}$
$n_{\text{fin}}, \text{mol}$	0.95×10^{-2}	—	2.05×10^{-2}	$+5.00 \times 10^{-4}$

the reaction by-product, sodium chloride, is a salt of a strong acid and a strong base, so it will not affect the pH of the solution; $V(\text{final solution}) = 0.3 \text{ dm}^3 + 0.0500 \text{ dm}^3 = 0.35 \text{ dm}^3$

$$c(\text{Na}_2\text{CO}_3)_{\text{fin}} = \left(\frac{0.95 \times 10^{-2}}{0.35} \right) \text{ mol dm}^{-3}, c(\text{NaHCO}_3)_{\text{fin}} = \left(\frac{2.05 \times 10^{-2}}{0.35} \right) \text{ mol dm}^{-3}$$

according to the Henderson–Hasselbalch equation:

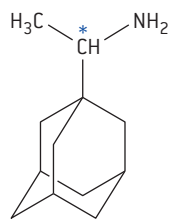
$$\text{pH}_{\text{fin}} = 10.3 + \log \frac{\frac{0.95 \times 10^{-2}}{0.35}}{\frac{2.05 \times 10^{-2}}{0.35}} = 10.3 + \log \frac{0.95}{2.05} \approx 10.3 - 0.3 = 10.0$$

D.5 Questions (page 750)

- in contrast to bacteria, viruses have no cellular structure (and thus have no nuclei, ribosomes, cytoplasm, or cell walls)
 - antiviral drugs work in several ways: interfere with virus replication (by becoming parts of viral RNA/DNA, altering viral DNA, or inhibiting the polymerase enzymes that build viral DNA); prevent viruses from entering cells (interfere with the attachment and uncoating stages); prevent viruses from leaving the cell;
 - possible responses can include the following: HIV replicates and mutates rapidly; HIV infects the very cells (lymphocytes) that are responsible for fighting viral infections; it is difficult to target HIV without damaging host cells; HIV can incorporate itself into the host DNA and remain dormant for many years;
- $\text{C}_{10}\text{H}_{17}\text{N}_1$
 - one primary (CH_3), seven secondary ($6 \times \text{CH}_2 + 1 \times \text{CH}-\text{NH}_2$), three tertiary ($3 \times \text{CH}$), and one quaternary (C) carbon atoms;
 - amantadine: tertiary (as the amino group is connected to a carbon atom that is connected to three other carbon atoms); rimantadine: secondary (as the amino group is connected to a carbon atom that is connected to two other carbon atoms);

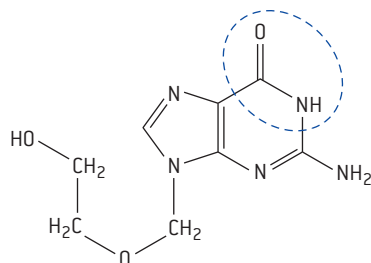


- d) amantadine: no chiral centres; rimantadine: one chiral centre;



- e) in contrast to bacteria, viruses lack cellular structure and their own metabolism, so there are fewer way to interfere with their functions; for the same reasons, viruses are not affected by antibiotics; viruses are not alive, so they cannot be “killed” by drugs; viruses multiply and mutate quickly, so viral infections are difficult to target at the early stages of their development;

3. a)



- b) the molecule of acyclovir contains several nitrogen atoms that can be protonated with acids; for example, the amino ($-\text{NH}_2$) group in acidic solutions transforms into an ammonium salt ($-\text{NH}_3^+$); protonated (ionized) groups form ion–dipole and hydrogen bonds with water, which increases the solubility of the drug;
- c) some drugs can be hydrolyzed (or otherwise deactivated) by gastric acid; other drugs have low bioavailability when taken orally; finally, an intravenous injection provides much faster effect than oral administration, as the injected drug quickly distributes around the body with the blood;

4. a) ester and amino groups

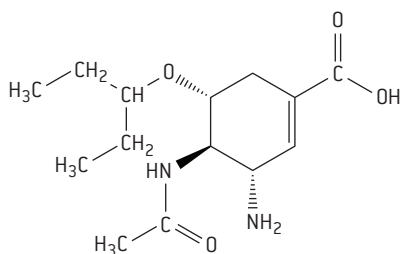
b) carboxyl and hydroxyl groups

c) ether and amido groups, carbon–carbon double bond (unsaturation)

d) zanamivir, as it has a greater number of polar groups (such as hydroxyl and carboxyl groups); these groups will form multiple hydrogen bonds with water, which will increase the solubility of the drug;

e) (i) an active metabolite is a pharmacologically active form of a drug after the drug has been processed (partly metabolized) by the body

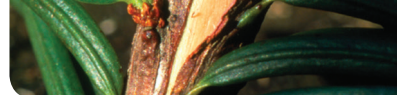
(ii)



5. a) four (all carbon atoms in the pentose ring)

b) retroviruses use reverse transcriptase enzymes to produce DNA strands from their RNA genomes (this process is the reverse of normal transcription)

c) in the host cell, zidovudine undergoes phosphorylation and produces non-standard nucleotides, which are mistakenly incorporated into RNA and DNA sequences; the enzymes produced from such altered templates are inactive and cannot be used for replicating viruses;



- d) viruses mutate quickly and eventually develop resistance to antiviral drugs; a “cocktail” of antivirals slows down this process and increases the overall efficiency of the treatment (the more antivirals are used at the same time, the greater the chance that the targeted virus will not be resistant to at least one of the drugs); a similar effect is achieved when a “cocktail” of antibiotics is used for treating resistant bacteria (refer to page 730);

e) refer to page 749

6. possible responses can include the following:

Sociocultural issue	Problems related to the issue
Condom use	Availability, cost, cultural resistance
Cultural factors	Ignorance, wishful thinking, misinformation, social stigma
Illegal activities	Drug use, prostitution, impact of wars
Resources / medical factors	Availability of medical services, cost of drugs, condom use
Orphans	Resources (state support), broken family life

7. possible responses can include the following: yes, as influenza has killed (and continues killing) more people than any other viral infection; no, as HIV treatment is expensive and must be continued until the rest of the patient’s life, which will become unsustainable if a significant percentage of the population is affected; yes, as influenza is highly contagious and can be transmitted via the respiratory route (through the air) while the transmission of HIV requires a sexual contact or blood transfusion and therefore can be easily prevented; no, as HIV is more widespread in certain countries and social groups, which produces various sociocultural issues (refer to answer 6);

D.6 Questions (page 757)

- a) in contrast to bacteria, viruses have no cellular structure (and thus have no nuclei, ribosomes, cytoplasm, or cell walls); viruses are smaller than bacteria; viruses are not living organisms, as they do not feed, grow, excrete, or have their own metabolism;

b) overuse of antibiotics has increased proportion of resistant bacteria; the use of penicillin in animal feedstock constantly introduces antibiotics into the environment and the human food chain (which gradually increases the proportion of resistant bacteria); the patients who do not complete their courses of antibiotics allow the most resistant bacteria to survive (and multiply after the course is terminated), and pass their resistance to next generations;
- possible responses can include the following: each individual has a right to protect his/her health, which includes the use of antibacterials in non-critical cases; the society has a right to protect its members from the overuse of antibiotics (that increases the bacterial resistance) and therefore restrict the production and distribution of these drugs; the benefits of antibacterial treatment to individual patients (faster recovery, increased productivity, better quality of life) can be outweighed by direct and indirect costs to the society (slower recovery and higher mortality rates among other patients, their decreased productivity and quality of life, costs associated with health services and the development of new drugs); any restrictions in the use of antibacterials will have very limited effect unless implemented at the international level;
- high-level waste has longer half-life (from thousands to billions of years) than low-level waste (typically up to several years); high-level waste is typically stored under water (in cooling ponds) for several years, then vitrified, encased in steel containers filled with concrete and buried deep underground; low-level waste is stored in shielded containers (or under water) until its activity drops to safe levels, after which it can be disposed of as normal (non-radioactive) waste;
- a) characteristics: low activity and short half-life; sources: gloves, paper towels, clothes, etc. that have been in proximity to radioactive materials; some radioactive materials themselves (solutions radiopharmaceuticals, smoke detectors, food/seed/plant irradiators, etc.); low-level waste can be also produced by supporting processes of the nuclear fuel cycle;



- b) methods: vitrification, encasing in concrete, burying in deep places; problems: radioactive materials may leak into water table, remain active for a very long time, may be released to the environment by earthquakes (or any other kinds of geological instability), can be potentially recovered and used by terrorists;
5. a) low-level waste: refer to answer 4 (a); high-level waste: main processes of the nuclear fuel cycle, nuclear weapons, radioisotope thermoelectric generators;
- b) (i) C
(ii) A
(iii) B
6. advantages: non-toxic, non-flammable, can be easily removed from mixture by evaporation, cheap and readily available; disadvantages: requires expensive equipment and high pressure (so an equipment failure might lead to an explosion);
7. supercritical carbon dioxide: refer to answer 6
- hydrogen peroxide: produces no toxic waste (as the only by-product is water), can be easily disposed of by catalytic or thermal decomposition into water and oxygen, strong and efficient oxidant with low molecular mass (so its use increases the atom efficiency of the whole technological process);
- molecular hydrogen: non-toxic, produces no toxic waste, can be easily disposed of by incineration or simply released to the atmosphere (where it will eventually oxidize to water), efficient reducing agent with low molecular mass (so it can potentially increase the atom efficiency of the technological process to nearly 100%);
8. a) hydroxyl group ($-\text{OH}$), carboxyl group ($-\text{COOH}$), carbon-carbon double bond ($\text{C}=\text{C}$);
- b) eight, as its molecule contains three stereocentres ($2 \times 2 \times 2 = 8$)
- c) plants need to be grown, which is expensive, takes up land and requires a long time; the extraction itself is a long and highly inefficient process (has low atom efficiency); it might also require toxic solvents and/or a lot of energy; microbiological production of shikimic acid has lower environmental impact than its extraction from plant material; it is faster, more efficient (in terms of atom economy), requires less space and energy; however, genetically modified bacteria must not be released to the environment (as it might have unpredictable consequences); bacteria also need nutrients for growth and must be constantly monitored; bacteria release waste by-products, which must be processed before disposal;
9. possible response can include the following: there has been a paradigm shift in the concept of efficiency (environmental impact and atom economy instead of just practical yield and cost of the product); “green” solvents and chemicals are gradually replacing traditional chemicals (such as chlorinated solvents and highly toxic reagents); the amounts of waste produced and energy used has decreased significantly; rigorous safety measures have reduced the number and severity of accidents; in some cases, the above measures have left less funds available for the research itself, which reduced the efficiency of drug development and raised the cost of pharmaceutical products;

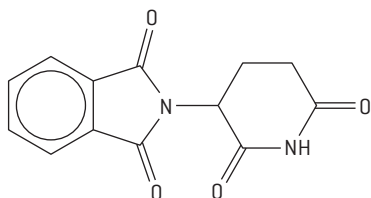
D.7 Questions (page 763)

1. a) semi-synthetic drugs are produced by traditional methods of organic chemistry using compounds from natural sources as starting materials
- b) extraction: refer to answer 8 (c) from sub-topic D.6; also, the extraction of Taxol involves the destruction of rare and endemic plant species (*Taxus brevifolia*), which makes this method ethically unacceptable;
- semi-synthetic production: has many advantages, including higher overall yield of the final product and the use of a common plant species (*Taxus baccata*) in a sustainable way (the leaves harvested from the tree are regenerated quickly); the main disadvantage is the use of traditional methods of organic chemistry, which involves toxic solvents and chemicals, requires a lot of energy and produces toxic waste;



- c) the structure of Taxol is very complex, and its molecule has 11 stereocentres, so the cost of its total synthesis on the industrial scale will be prohibitively high

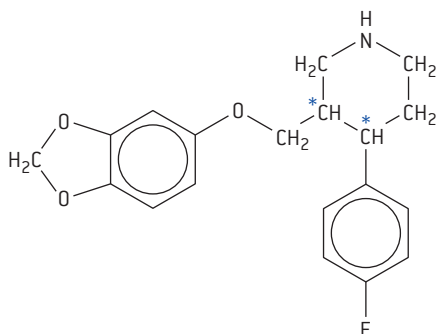
2. a)



b) equimolar mixture of a pair of enantiomers

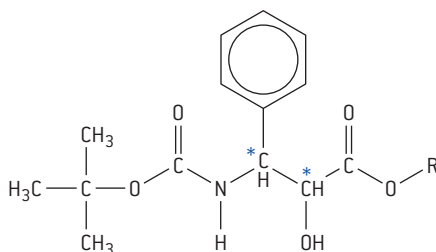
- c) possible response can include the following: the active and allosteric sites of enzymes and cell receptors are chiral, so the drug must have correct stereochemical configuration to be pharmacologically active; if one enantiomer of the drug fits into the active or allosteric site of one enzyme (or cell receptor), another enantiomer might not fit there or fit into the active or allosteric site of another enzyme (or cell receptor); therefore, enantiomers may have very different physiological properties (one enantiomer may cause the desired effect while the other enantiomer can produce side-effects or be biologically inactive); enantiomers might interconvert in the human body or when combined with other substances, so this possibility must be always taken into account;

3. a)



- b) chiral auxiliaries are themselves chiral; when a chiral auxiliary is attached to a non-chiral molecule, it affects its further chemical transformations (so when further chiral centres are introduced, only specific diastereomers are formed); when the desired isomer is synthesized, the chiral auxiliary is detached from the molecule (and sometimes can be recycled);

4. a)



b) four (as each chiral centre can have two configurations, so $2 \times 2 = 4$)

c) refer to answer 2 (c)

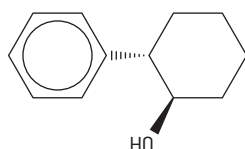
5. a) hydrolysis (nucleophilic substitution)

b) left: ester group (ethanoate); right: hydroxyl group;

c) because there are other hydroxyl groups in the molecule, so they will also react with ethanoic acid, and a mixture of many different products will be obtained

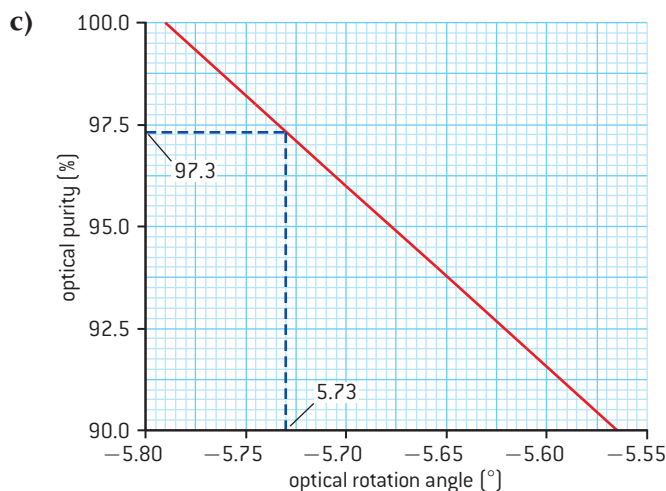
d) nine

6. a)





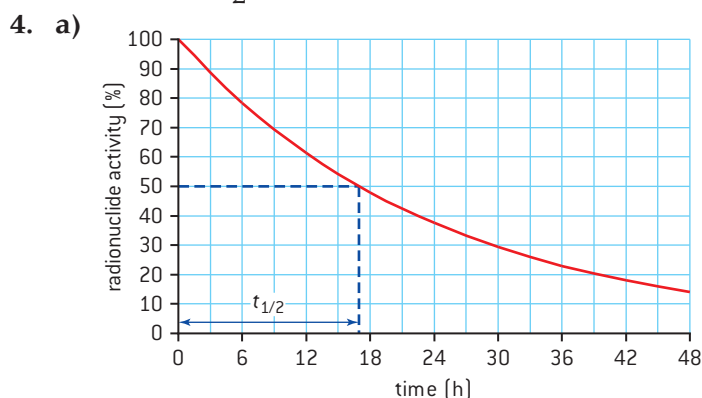
- b) under identical conditions, both enantiomers (of the same compound) will rotate plane-polarized light by the same angle but in opposite directions; the angle of rotation is unique for each compound (i.e., enantiomers of different compounds will rotate plane-polarized light by different angles); polarimeter can both determine the direction of rotation (clockwise or counter-clockwise) and measure the angle of rotation, therefore, a polarimeter can be used to identify specific enantiomers of the same compound (by the direction of rotation) or pure enantiomers of unknown compounds (by the degree of rotation);



according to the calibration curve, the rotation angle of 5.73° corresponds to the optical purity of approximately 97.3%;

D.8 Questions (page 774)

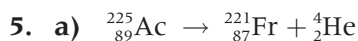
- refer to pages 765 and 771
- refer to page 765
 - damage to growing/multiplying cells that results in hair loss, skin and nail damage, nausea, fatigue, sterility, possibility of secondary cancers
- after each half-life, the amount of the radionuclide is reduced by half, so after n half-lives, it will be reduced 2^n times, therefore, after 5 half-life periods, there will be $\frac{1}{2^5} \approx 100\% \approx 3\%$ of the initial radionuclide left;
 - similarly, $\frac{1}{2^{10}} \times 100\% \approx 0.1\%$



- b) according to the plot, $t_{1/2} \approx 17$ h
- c) we can use any two points from the table (for example, $t_0 = 0$ h and $t = 42$ h); according to the

formulae on page 772, $\lambda \frac{\ln \frac{N_0}{N}}{t}$ and $t_{1/2} \approx \frac{0.693}{\lambda}$, so:

$$\lambda \frac{\ln \frac{100}{18}}{42} \approx 0.0408 \text{ h}^{-1} \text{ and } t_{1/2} = \frac{0.693}{0.0408} \approx 17 \text{ h}$$



b) refer to page 768

c) alpha particles have large mass and therefore release a lot of energy upon collisions with other particles; due to their large size and charge, alpha particles are also more likely to collide with other particles, so they have low penetrating power but cause extensive local damage;

6. a) beta particles have low penetrating power, so they must be produced near or within cancer cells; an attempt to use beta particles in external radiotherapy would cause extensive damage to the patient's skin, which would block most of these particles;

b) according to the formulae on page 772:

$$\lambda \approx \frac{0.693}{t_{1/2}} = \frac{0.693}{6.6} = 0.105 \text{ day}^{-1}$$

$$N = N_0 e^{-\lambda t} = 7 \text{ mg} \times e^{-0.105 \times 30} \approx 0.3 \text{ mg}$$

7. a) refer to page 768

b) refer to page 769



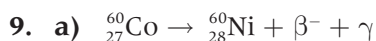
b) total preparation time is $40 + 5 = 45$ min; according to the formulae on page 772:

$$\lambda \frac{0.693}{t_{1/2}} = \frac{0.693}{10} = 0.0693 \text{ min}^{-1}$$

$$N = N_0 e^{-\lambda t} = 100\% \times e^{-0.0693 \times 45} \approx 4.4\%$$

after 45 min, only 4.4% of ${}^{13}\text{N}$ will remain in the injection solution, so the percentage of decayed ${}^{13}\text{N}$ will be $100\% - 4.4\% = 95.6\%$

c) all known positron emitters decay very rapidly (have short half-life periods), so they cannot be delivered to remote areas and must be prepared on the spot



b) according to the second formula on page 772

$$\lambda \approx \frac{0.693}{t_{1/2}} = \frac{0.693}{5.3} \approx 0.131 \text{ year}^{-1}$$

$$N = N_0 e^{-\lambda t} = N_0 e^{-0.131 \times 10} \approx 0.27 N_0$$

therefore, the activity will decrease $\frac{N_0}{N} = \frac{1}{0.27} \approx 3.7$ times

c) if 99.99% of cobalt-60 decays, 0.01% of the isotope will remain, so $N = N_0 \times 10^{-4}$ and

therefore $N_0 = N \times 10^4$; according to the last formula on page 772, $t = \frac{\ln(10^4)}{0.131} \approx 70$ years;

D.9 Questions (page 783)

1.	Peak	A	B	C	D	E	F	G
	Hydrogen atom responsible	7	4	6	3	2	5	1

2. a) two

b) both are singlets (no splitting)

c) aspirin will probably have two peaks in this region (due to the two C=O groups in its molecule), however, if the absorptions of these two groups are close to each other, they might overlap and produce one wider and/or stronger peak;

ibuprofen will have one peak in this region (because it has only one C=O group); if the two peaks of aspirin overlap, then the single peak of ibuprofen will look narrower and/or less intensive;

3. $c = 125 \times 0.60 \text{ } \mu\text{mol dm}^{-3} = 75 \text{ } \mu\text{mol dm}^{-3}$



4. a) the mixture is shaken with water and an organic solvent (which is immiscible with water) in a separation funnel; the polar compound dissolves in water, the non-polar compound dissolves in the organic solvent; The emulsion is allowed to settle until two layers are formed; each layer is run into a separate beaker; the solvent and water are evaporated, leaving the two components of the mixture in different beakers;

b) $P_c(X) = \frac{[X(\text{org})]}{[X(\text{aq})]}$

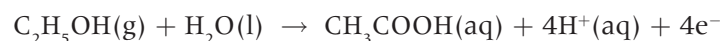
- c) since the volumes of the aqueous solution and octan-1-ol are equal, the concentrations of X in both layers are proportional to its amounts; if $0.012 \text{ mol dm}^{-3}$ of X is left in the aqueous phases, then $0.46 - 0.012 = 0.448 \text{ mol dm}^{-3}$ of X has been passed into octan-1-ol; therefore,

$$P_c(X) = \frac{0.488}{0.012} \approx 41$$

$$\log P(X) = \log 41 \approx 1.61$$

5. a biological material (or its extract) is injected into a GC or HPLC column; the components are separated according to their volatility (GC) or solubility (HPLC) and affinity to the stationary phase; the presence of a banned substance in the body can be detected by its retention time and confirmed by mass spectroscopy (MS); in an MS detector, the substance is vaporized and ionized. Ions are accelerated by electric field and deflected by magnetic field according to their mass to charge ratios (m/z); each substance produces a unique pattern of ionized fragments, which can be detected and compared with a library of known substances;

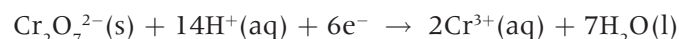
6. a) oxidation:



or



reduction:



- b) reduced, as chromium gains electrons and its oxidation number decreases from +6 to +3
- c) fuel cell: ethanol is oxidised by the atmospheric oxygen on the surface of a platinum electrode; the electric current produced is proportional to the concentration of ethanol in the breath, which can be related to the suspect's blood alcohol concentration (BAC);

IR spectroscopy: the presence of alcohol in the breath is detected by the absorption of infrared light at certain wavelengths, which is caused by the C–H and C–O bonds in ethanol; IR radiation alternatively passes through two chambers; one chamber contains a breath sample, another contains atmospheric air; the difference in absorption between the chambers is converted to the ethanol concentration using the Beer–Lambert law;

7. a) from orange to green

- b) ethanoic (acetic) acid or ethanal (acetaldehyde)

- c) blood sample: gas chromatography (GC) or high performance liquid chromatography (HPLC); ethanol is separated from other components of the blood on a column; the peak of ethanol is identified by its retention time and/or mass-spectroscopy (MS); the amount of ethanol in the blood is proportional to the area under its peak; the exact blood alcohol level (BAC) is determined by comparing the peak area with that of a known sample (or using a calibration curve);

intoximeter: refer to answer 6 (c);

8. possible responses can include the following: the use of performance-enhancing drugs in sport has decreased due to constantly improving detection techniques; numerous doping cases against prominent athletes (such as Lance Armstrong) has affected the public attitude toward the use of drugs in sport and professional sport itself; to avoid detection of banned substances, some



athletes use progressively sophisticated (and therefore expensive) techniques, which may get them involved into other unlawful activities (illegal betting, match-fixing, etc.); outside professional sport, an increasing number of people have to provide samples of their biological materials for routine drug tests, which is often beneficial for the society but limits personal freedom of individuals.

Note: Some of the questions in this textbook are from past exam papers and have responses available in the IB questionbank.